

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark
Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

29 September 1998 (29.09.98)

International application No.

PCT/NO98/00051

Applicant's or agent's file reference

AB/84746

International filing date (day/month/year)

20 February 1998 (20.02.98)

Priority date (day/month/year)

20 February 1997 (20.02.97)

Applicant

WENDELBO, Rune et al

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

04 September 1998 (04.09.98)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Lazar Joseph Panakal

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To: **7 SEPT 1998**
BENDIKSEN, Asbjørn
 Bryn & Aarfлот a/s
 P.O. Box 449 Sentrum
 N-0104 Oslo
 NORVEGE

Date of mailing (day/month/year)

27 August 1998 (27.08.98)

Applicant's or agent's file reference

AB/84746

IMPORTANT NOTICE

International application No.

PCT/NO98/00051

International filing date (day/month/year)

20 February 1998 (20.02.98)

Priority date (day/month/year)

20 February 1997 (20.02.97)

Applicant

SINVENT_AS et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
 AU, BR, CA, CN, EP, IL, JP, KP, KR, NO, PL, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL, AM, AP, AT, AZ, BA, BB, BG, BY, CH, CU, CZ, DE, DK, EA, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IS, KE,
 KG, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NZ, OA, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ,
 TM, TR, TT, UA, UG, UZ, VN, YU, ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 48.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
 27 August 1998 (27.08.98) under No. WO 98/36826

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
 34, chemin des Colombettes
 1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.36

Authorized officer

J. Zahra

Telephone No. (41-22) 338.83.38

Continuation of Form PCT/IB/308

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF
THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

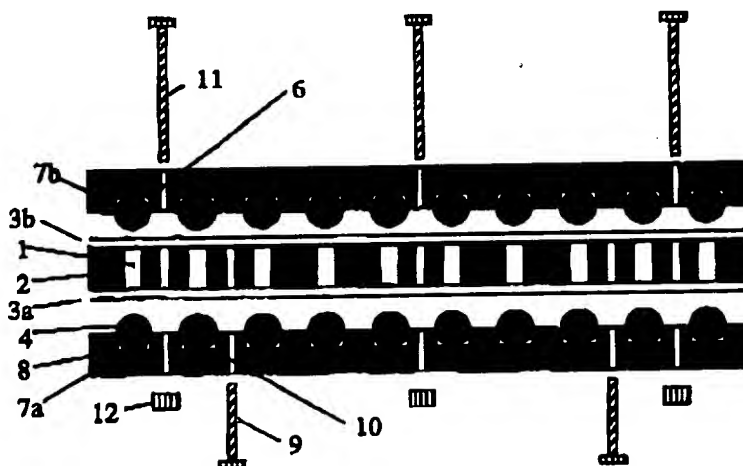
Date of mailing (day/month/year) 27 August 1998 (27.08.98)	IMPORTANT NOTICE
Applicant's or agent's file reference AB/84746	International application No. PCT/NO98/00051
<p>The applicant is hereby notified that, at the time of establishment of this Notice, the time limit under Rule 46.1 for making amendments under Article 19 has not yet expired and the International Bureau had received neither such amendments nor a declaration that the applicant does not wish to make amendments.</p>	

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: B01J 3/00, C30B 29/34		A1	(11) International Publication Number: WO 98/36826
			(43) International Publication Date: 27 August 1998 (27.08.98)
(21) International Application Number: PCT/NO98/00051		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GR, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 20 February 1998 (20.02.98)			
(30) Priority Data: 970788 20 February 1997 (20.02.97) NO			
(71) Applicant (for all designated States except US): SINVENT AS (NO/NO); Strindveien 4, N-7034 Trondheim (NO).			
(72) Inventors; and (75) Inventors/Applicants (for US only): WENDELBO, Rune (NO/NO); Peer Gyntsv. 2, N-0854 Oslo (NO). AKPO-RIAYE, Duncan, E. (NO/NO); Kristina Bonnevies vei 15, N-0592 Oslo (NO). KARLSSON, Arne (NO/NO); Grågåsvæien 1c, N-1187 Oslo (NO). DAHL, Ivar, Martin (NO/NO); Kongsberggata 6, N-0468 Oslo (NO).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(74) Agent: BENDIKSEN, Asbjørn; Bryn & Aarflot a/s, P.O. Box 449 Sentrum, N-0104 Oslo (NO).			

(54) Title: MULTIAUTOCCLAVE FOR COMBINATORIAL SYNTHESIS OF ZEOLITES AND OTHER MATERIALS



(57) Abstract

The invention relates to a multiautoclave and details of its design and a method for automated synthesis of zeolites in said multiautoclave and, furthermore, application of the multiautoclave for an automated synthesis which is optimized simultaneously with regard to several synthesis parameters in the synthesis of zeolites. The multiautoclave consists typically of a pressure vessel/autoclave lined with an inert material with from 10 to 10.000 small, separated chambers, each typically having a volume of 0,2-2 ml, the chambers preferably being formed as through-going perforations in a central block and the perforations are sealed by means of balls, septa, stoppers or such which are placed at the bottom and top of each through-going perforation, and metal plates are placed over and under the Teflon plate so that the closing mechanism is pressed against the edges of the perforations in the Teflon plate with sufficient load to enable the chambers to be filled with aqueous mixtures and to be heated to 200 °C without the occurrence of leakage. Top and bottom plates and closing mechanisms can be integrated so that all the perforations are sealed simultaneously when these are placed at the top and bottom sides of the central block.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00051

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 3/00, C30B 29/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J, C01B, C30B, F17C, F16J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5112574 A (NIKKI HORTON), 12 May 1992 (12.05.92), column 3, line 65 - column 4, line 4, figures 1-4,9, abstract --	1-17
Y	US 5505916 A (BERNIE B. BERRY, JR.), 9 April 1996 (09.04.96), column 6, line 3 - line 7, figure 1 --	1-17
A	US 5400741 A (GEORGE T. DETITTA ET AL), 28 March 1995 (28.03.95), figures 1-7 --	1-17
A	US 5531185 A (KOJI ASANO ET AL), 2 July 1996 (02.07.96), figures 8-9, abstract --	1-12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 June 1998

Date of mailing of the international search report

30-06-1998

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Mårten Hulthén
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00051

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5096676 A (ALEXANDER MCPHERSON ET AL), 17 March 1992 (17.03.92), figures 1-2, abstract --	1-17
A	EP 0553539 A1 (SCHERING CORPORATION), 4 August 1993 (04.08.93), figures 1-7 --	1-17
P,A	EP 0780496 A1 (DORNIER GMBH), 25 June 1997 (25.06.97), figure 3 -- -----	1-17

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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INTERNATIONAL SEARCH REPORT
 Information on patent family members

09/06/98

International application No.

PCT/NO 98/00051

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
US	5112574	A	12/05/92	NONE	
US	5505916	A	09/04/96	NONE	
US	5400741	A	28/03/95	NONE	
US	5531185	A	02/07/96	JP 7185313 A	25/07/95
US	5096676	A	17/03/92	NONE	
EP	0553539	A1	04/08/93	AU 2764492 A	03/05/93
				CA 2120744 A	15/04/93
				EP 0607262 A	27/07/94
				JP 7500806 T	26/01/95
				MX 9205727 A	01/04/93
				US 5221410 A	22/06/93
				WO 9307311 A	15/04/93
EP	0780496	A1	25/06/97	DE 19548742 C	28/05/97

jfb 30/4

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

GÖRBITZ, Johan H.
BRYN & AARFLOT A/S
P.O. Box 449 Sentrum
0104 Oslo
NORVEGE

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year)

22.05.99

Applicant's or agent's file reference
G/84746

IMPORTANT NOTIFICATION

International application No.
PCT/NO98/00051

International filing date (day/month/year)
20/02/1998

Priority date (day/month/year)
20/02/1997

Applicant
SINVENT AS et al

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

European Patent Office
D-80288 Munich
Tel. (+49-89) 23999-0 Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer

Gregoire, J-P

Tel. (+49-89) 2399-8041




PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference G/84746		FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NO98/00051	International filing date (day/month/year) 20/02/1998	Priority date (day/month/year) 20/02/1997	
International Patent Classification (IPC) or national classification and IPC B01J3/00			
Applicant SINVENT AS et al			
<p>1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 3 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the International application VIII <input checked="" type="checkbox"/> Certain observations on the International application 			
Date of submission of the demand 04/09/1998		Date of completion of this report 1998	
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465		Authorized officer Buesing, G Telephone No. (+49-89) 2399 8356	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO98/00051

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-17 as originally filed

Claims, No.:

1-17 as received on 12/01/1999 with letter of 08/01/1999

Drawings, sheets:

1/7-7/7 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO98/00051

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Yes: Claims 1, 3 - 17
	No: Claims 2
Inventive step (IS)	Yes: Claims
	No: Claims 1, 3 - 17
Industrial applicability (IA)	Yes: Claims 1 - 17
	No: Claims

2. Citations and explanations**see separate sheet****VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

INTERNATIONAL PRELIMINARY

International application No. PCT/NO98/00051

EXAMINATION REPORT - SEPARATE SHEET

Section V:

1. Claims 1 and 2 define a multiautoclave reactor vessel in broad terms. Basically, the reactor vessel has a central block with a multitude of perforations or cavities, cover means, sealing means and locking means.

It is observed that claim 2 has to be considered as independent because it does not contain a feature which is additional to claim 1 but rather is an alternative feature (permanently closed cavities instead of through-going perforations).

2. According to the description, the invention is more specifically directed to a multiautoclave reactor which should withstand temperatures in the range between 100 and 250°C (page 4, line 34) and elevated pressures (page 3, lines 10 - 12) the range of which has not been specified in the description. Typical reactor volumes are indicated on page 6, line 36.
3. From the documents cited in the international search report, US-A-5112574 (hereinafter D1) represents the closest prior art. As seen in Fig. 9 of D1, the array of wells 18 forms a central block with a multitude of cavities permanently closed at one end and with cover means, operatively associated with sealing means, for engagement with said central block to seal the open ends of said cavities. The sealing means, which are operatively associated with the cover means, form a "pressure tight" seal when said cover means is brought into position by a locking means (reference numeral 23 in Fig. 1).

The subject-matter of claim 2 is anticipated by D1.

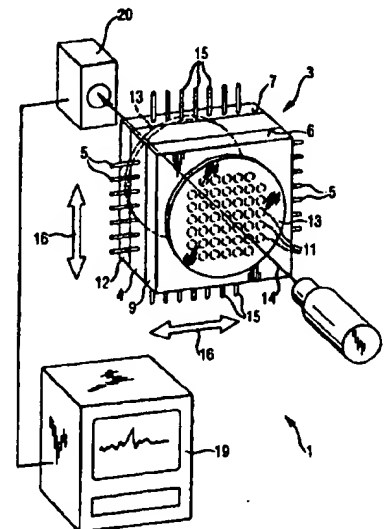
4. It is not apparent how the use of through-going perforations, as in claim 1, or other features of the dependent claims or the description could support an inventive step. Therefore, it is not seen which part of the application could serve as a basis for a claim defining new and inventive subject-matter.

Section VIII:

1. It is noted that the reference to "elevated pressure" in claim 1 is vague and indefinite in the absence of a definition of a suitable pressure range and is merely interpreted as any pressure above atmospheric.


 INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
 INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ⁶ : G01N 31/10	A1	(11) Internationale Veröffentlichungsnummer: WO 98/07026 (43) Internationales Veröffentlichungsdatum: 19. Februar 1998 (19.02.98)
(21) Internationales Aktenzeichen: PCT/EP97/04369 (22) Internationales Anmeldedatum: 12. August 1997 (12.08.97) (30) Prioritätsdaten: 196 32 779.2 15. August 1996 (15.08.96) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): HOECHST RESEARCH & TECHNOLOGY DEUTSCH- LAND & CO. KG [DE/DE]; Brüningstrasse 50, D-65929 Frankfurt am Main (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): WINDHAB, Norbert [DE/DE]; Akazienstrasse 28, D-65795 Hattersheim (DE). MICULKA, Christian [DE/DE]; Gebeschusstrasse 36, D-65929 Frankfurt am Main (DE). HOPPE, Hans-Ulrich [DE/DE]; Amselweg 11, D-65929 Frankfurt am Main (DE).		(81) Bestimmungsstaaten: AU, CA, JP, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht.</i> <i>Vor Ablauf der für Änderungen der Ansprüche zugelassenen</i> <i>Frist. Veröffentlichung wird wiederholt falls Änderungen</i> <i>eintreffen.</i>
(54) Title: PROCESS AND FACILITY FOR EXAMINING CHEMICAL REACTIONS IN MINIATURIZED REACTORS ARRANGED PARALLEL TO EACH OTHER		
(54) Bezeichnung: VERFAHREN UND VORRICHTUNG ZUM UNTERSUCHEN VON CHEMISCHEN REAKTIONEN IN PARALLEL GESCHALTETEN, MINIATURISIERTEN REAKTOREN		
(57) Abstract <p>The invention pertains to a process for examining chemical reactions in the presence of potentially catalytical substance, wherein reactions are triggered in miniaturized reactors arranged parallel to each other and the nature and amount of the reaction mixture are analyzed during the reaction time. A facility involving reactors provided with inlet pipes and by-passes has miniaturized reactors with volumes of 0,001 cm³ to 1 cm³. Said invention allows for effecting a large number of reactions under virtually identical conditions and with a relatively low amount of substance and samples, at an attractive cost and in a reproducible manner, and simultaneous spectroscopic analysis. It also provides a means of using for industrial catalyst screening the possibilities discussed in relation to combinatorial chemistry. Choosing identical samples and other different reaction conditions ensures optimized parallel reactions.</p> <p>(57) Zusammenfassung Gegenstand der Erfindung ist ein Verfahren zur Untersuchung von chemischen Reaktionen in Gegenwart von potentiell katalytischen Substanzen, bei dem man die Reaktionen parallel in Reaktoren durchführt, dadurch gekennzeichnet, daß man die Reaktionen in miniaturisierten Reaktoren durchführt und das Reaktionsgemisch während der Reaktionszeit nach Art und Menge analysiert. Gegenstand der Erfindung ist außerdem eine Vorrichtung mit Reaktoren, die mit Zu- und Ableitungen versehen sind, dadurch gekennzeichnet, daß die Reaktoren miniaturisiert sind, bei einem Volumen aus dem Bereich von 0,001 cm³ bis 1 cm³. Die Vorteile liegen im wesentlichen darin, daß eine Vielzahl von Reaktionen unter praktisch identischen Bedingungen und mit vergleichsweise geringen Substanz- und Probenmengen schnell, kostengünstig und reproduzierbar durchgeführt und dabei gleichzeitig spektroskopisch untersucht werden kann. Sie bietet damit die Möglichkeit, die im Zusammenhang mit der kombinatorischen Chemie diskutierten Möglichkeiten für ein industrielles Katalysatorscreening einzusetzen. Durch die Wahl identischer Proben und unterschiedlicher sonstiger Reaktionsbedingungen kann eine parallele Reaktionsoptimierung durchgeführt werden.</p>		



LEDIGLICH ZUR INFORMATION

Codes zur Identifizierung von PCT-Vertragsstaaten auf den Kopfbögen der Schriften, die internationale Anmeldungen gemäss dem PCT veröffentlichen.

AL	Albanien	ES	Spanien	LS	Lesotho	SI	Slowenien
AM	Armenien	FI	Finnland	LT	Litauen	SK	Slowakei
AT	Österreich	FR	Frankreich	LU	Luxemburg	SN	Senegal
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BB	Barbados	GH	Ghana	MG	Madagaskar	TJ	Tadschikistan
BE	Belgien	GN	Guinea	MK	Die ehemalige jugoslawische Republik Mazedonien	TM	Turkmenistan
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CA	Kanada	IT	Italien	NE	Niger	UZ	Usbekistan
CF	Zentralafrikanische Republik	JP	Japan	NL	Niederlande	VN	Vietnam
CG	Kongo	KE	Kenia	NO	Norwegen	YU	Jugoslawien
CH	Schweiz	KG	Kirgisistan	NZ	Neuseeland	ZW	Zimbabwe
CJ	Côte d'Ivoire	KP	Demokratische Volksrepublik Korea	PL	Polen		
CM	Kamerun	KR	Republik Korea	PT	Portugal		
CN	China	KZ	Kasachstan	RO	Rumänien		
CU	Kuba	LC	St. Lucia	RU	Russische Föderation		
CZ	Tschechische Republik	LI	Liechtenstein	SD	Sudan		
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DK	Dänemark	LR	Liberia	SG	Singapur		
EE	Estland						

Beschreibung

Verfahren und Vorrichtung zum Untersuchen von chemischen Reaktionen in parallel geschalteten, miniaturisierten Reaktoren

Die Erfindung betrifft ein Verfahren zur Untersuchung von chemischen Reaktionen in Gegenwart von potentiell katalytischen Substanzen, bei dem man die Reaktionen parallel in Reaktoren durchführt. Die Erfindung betrifft weiterhin eine Vorrichtung, insbesondere zur Durchführung dieses Verfahrens, wobei die Vorrichtung mehrere, parallel geschaltete Reaktoren aufweist, die mit Zu- und Ableitungen versehen sind.

Verfahren und Vorrichtungen der genannten Art sind bekannt und werden unter anderem bei der Suche nach Katalysatoren zur heterogenen oder homogenen Katalyse technischer, chemischer Prozesse eingesetzt.

In jüngster Zeit ermöglichen es jedoch neue Techniken, Substanzen in hoher Zahl herzustellen, die potentielle Katalysatoren für eine Vielzahl von chemischen Prozessen sein könnten (P. G. Schultz et al., Science 1995, 1738). Die Untersuchung dieser Vielzahl von potentiellen Katalysatoren ist mit den herkömmlichen seriellen Screening-Verfahren kaum mehr möglich, da diese Screening-Verfahren bezüglich Durchsatz und analytischer Auflösung sowie in der Reproduzierbarkeit limitiert sind. Oft werden für reines Aktivitätsscreening völlig unzureichend integrale Effekte wie Erwärmung des Katalysators etc. ohne direkte Produktgemisch- bzw. Effektivitätsanalyse herangezogen. Außerdem stellen die Optimierung der Bedingungen zur Katalysatoraktivierung und Prozessführung besondere Anforderungen an quantitative, analytische Verfahren und an die Reproduzierbarkeit der Reaktionsbedingungen.

Der Erfindung lag daher die Aufgabe zugrunde, ein kostengünstiges Verfahren oder eine kostengünstige Vorrichtung zu entwickeln, womit man eine Vielzahl

2

von chemischen Reaktionen in kurzer Zeit untersuchen kann und dabei reproduzierbare, qualitative und quantitative Daten bezüglich der Zusammensetzung der unterschiedlichen Reaktionsgemische und Reaktionsprodukte gewinnen kann.

Gelöst wird diese Aufgabe durch ein Verfahren der eingangs genannten Art, das dadurch gekennzeichnet ist, daß man die Reaktionen in miniaturisierten Reaktoren durchführt und das Reaktionsgemisch oder die Reaktionsprodukte während der Reaktionszeit nach Art und Menge analysiert.

Die Aufgabe wird außerdem durch eine Vorrichtung der genannten Art gelöst, die dadurch gekennzeichnet ist, daß die Reaktoren miniaturisiert sind, bei einem Volumen aus dem Bereich von $0,001 \text{ cm}^3$ bis 1 cm^3 .

Gegenstand der Erfindung ist somit ein Verfahren zur Untersuchung von chemischen Reaktionen in Gegenwart von potentiell katalytischen Substanzen, bei dem man die Reaktionen parallel in Reaktoren durchführt, dadurch gekennzeichnet, daß man die Reaktionen in miniaturisierten Reaktoren durchführt und das Reaktionsgemisch während der Reaktionszeit nach Art und Menge analysiert.

Gegenstand der Erfindung ist außerdem eine Vorrichtung, insbesondere zur Durchführung dieses Verfahrens, wobei die Vorrichtung mehrere, parallel geschaltete Reaktoren aufweist, die mit Zu- und Ableitungen versehen sind, dadurch gekennzeichnet, daß die Reaktoren miniaturisiert sind, bei einem Volumen aus dem Bereich von $0,001 \text{ cm}^3$ bis 1 cm^3 .

Besondere Ausführungsformen bzw. Ausgestaltungen der Erfindung ergeben sich aus den jeweiligen Unteransprüchen. Es können auch einzelne oder mehrere der in den Ansprüchen genannten Einzelmerkmale jeweils für sich

erfindungsgemäße Lösungen darstellen, und es sind auch die Merkmale innerhalb der Anspruchskategorien beliebig kombinierbar.

Eine besondere Ausführungsform des erfindungsgemäßen Verfahrens ist dadurch gekennzeichnet, daß man die Reaktionsedukte laufend den Reaktoren zuführt und die Reaktionsprodukte laufend aus den Reaktoren abführt. Die Batch-Fahrweise ist aber ebenfalls möglich.

Eine weitere besondere Ausführungsform ist dadurch gekennzeichnet, daß man Edukte verwendet, die mindestens teilweise mit Isotopen markiert sind, bevorzugt mit Deuterium (^2H) oder schweren Sauerstoff (^{18}O) oder schweren Kohlenstoff (^{13}C) oder Mischungen davon. Diese erzeugen charakteristische Spektralverschiebungen in Rotations-Schwingungsspektren, was neben der Reaktionswegemarkierung durch Eduktgemischvarianten zu neuen, interessanten Reaktionen bzw. Reaktionsprodukten führen kann und kleinere Nebenproduktanteile systematisch kontrastiert.

Es können auch einzelnen oder zu Gruppen zusammengefaßten Reaktoren unterschiedliche Eduktgemische zugeführt werden, um so mit den Methoden der kombinatorischen Chemie eventuell vorhandene Synergien zu erkennen oder zu entdecken.

Die Edukt-, Reaktions- bzw. Produktgemische können mittels spektroskopischer Analyse, bevorzugt mittels Infrarotspektroskopie (IR), besonders bevorzugt mittels Fourier IR-Spektroskopie zu beliebigen Zeitpunkten des Reaktionsverlaufs nach Art und Menge der enthaltenen Substanzen analysiert werden. Andere spektroskopische Methoden wie Laser- oder UV-Spektroskopie sind zur Untersuchung ebenfalls geeignet. Das Verfahren kann bei unterschiedlichen Temperaturen und Drücken durchgeführt werden, bei Temperaturen aus dem Bereich von $-50\text{ }^{\circ}\text{C}$ bis einschließlich $600\text{ }^{\circ}\text{C}$, bevorzugt von Raumtemperatur bis $500\text{ }^{\circ}\text{C}$, oder bei unterschiedlichen Drücken, bei Absolutdrücken von 10^{-3} bis 10^3 bar, bevorzugt von 10^{-2} bis 200 bar. Die gewonnenen Daten können dann einer umfassenden Parameter- und

Datenanalyse zugeführt werden.

Die Erfindung ist weiter dadurch gekennzeichnet, daß die Reaktionen in Gegenwart eines heterogenen oder homogenen Katalysators durchgeführt werden können und daß das Screening der katalytischen Aktivität (d.h. Produktnachweis) und Selektivität (Hauptproduktverteilung) von Katalysatormengen kleiner als 10 mg, bevorzugt kleiner als 1 mg, in einem Reaktor möglich ist.

In einer besonderen Ausgestaltungsform der erfindungsgemäßen Vorrichtung können in einem Block mehrere, voneinander getrennte, miniaturisierte Reaktoren angeordnet sein. Das Volumen dieser Reaktoren kann im Bereich von $0,001 \text{ cm}^3$ bis 1 cm^3 , bevorzugt von $0,01 \text{ cm}^3$ bis $0,5 \text{ cm}^3$, besonders bevorzugt von $0,05 \text{ cm}^3$ bis $0,2 \text{ cm}^3$ sein. In einer weiteren bevorzugten Ausgestaltungsform der erfindungsgemäßen Vorrichtung sind die Reaktoren als quadratisches oder rechteckiges Muster in einem Metallblock angeordnet, der quader- oder würfelförmig sein kann. Der Metallblock kann mit Heizblock- oder Kühlelementen versehen sein und kann in der Nähe eines jeden Reaktors mit einem Temperaturfühler ausgestattet sein. Dies ermöglicht eine kontrollierte und reproduzierbare Temperaturführung. Beispielsweise kann dadurch ein definierter Temperaturgradient über den Metallblock eingestellt werden. Die Reaktoren sind vorteilhafterweise in einer Ebene, die parallel zu einer Oberfläche des Quaders liegt, angeordnet. Die Zu- und Ableitungen der einzelnen Reaktoren liegen vorteilhafterweise zumindest teilweise senkrecht zu dieser Ebene. Sie können in dem Metallblock als durchgehende Bohrungen ausgeführt sein. Die Reaktoren können als Bohrungen ausgeführt sein. Die Zahl der Reaktoren in einem Block kann größer sein als 20, bevorzugt größer als 40, besonders bevorzugt größer als 100, ganz besonders bevorzugt größer als 200. Mit diesen Reaktoren können unter definierten Reaktionsbedingungen kleine Menge potentieller Katalysatoren (im folgenden auch Proben genannt) parallel, d.h. gleichzeitig mit Edukt bzw. Eduktgemischen in flüssiger und/oder in gasförmiger Form diskontinuierlich oder kontinuierlich in Kontakt und zur

Reaktion gebracht werden. Eine Automatisierung der erfindungsgemäßen Vorrichtung ist möglich, insbesondere kann das Beschicken der Reaktoren mit Katalysatoren automatisch, bevorzugt durch einen Laborroboter oder einen Pipettierer erfolgen.

In einer weiteren besonderen Ausgestaltungsform sind die miniaturisierten Reaktoren in dem Metallblock als 4 mm-Bohrungen ausgeführt und so angeordnet, daß sie durch 2,5-mm-Kapillarbohrungen mit unterschiedlichen Edukt- und Inertgasen beströmt werden können. Die Gase gelangen anschließend in einen Abstandshalter, vorzugsweise eine Distanzplatte, die auf den Metallblock aufgesetzt ist und in der sich die Bohrungen des Metallblocks fortsetzen. Die Anordnung aus Metallblock und Abstandshalter ist mit einer gängigen Küvettenbohrung versehen, in der die Gase spektroskopisch analysiert werden können. Dazu ist die Bohrung an beiden Enden mit einem transparenten Fenster verschlossen. Will man mit Infrarotspektroskopie analysieren, verwendet man bevorzugt Fenster aus 1-1-1-Silicium, NaCl, KBr, Ge, ZnSe oder KSR5. Zur Analyse wird ein kollimierter Analysestrahl, bei IR-Spektroskopie ein Infrarotstrahl, bevorzugt spiefelfrei aus einem Interferometer ausgekoppelt und durch Trockengas-gespülten Raum durch die Küvettenbohrung auf einen dahinter liegenden Detektor gelenkt. Die Küvettenbohrung kann beispielsweise 5 mm dick sein. Durch die Wahl eines geeigneten dicken Abstandhalters kann die Länge der Küvettenbohrung zwischen wenigen cm (1-10) und mehreren 10 cm (10-50) gewählt werden, je nach Reaktionsbedingungen und Reaktionstyp. Zur Aufnahme der Spektren kann der Analysestrahl mittels einer Ablenkvorrichtung nacheinander durch alle Küvettenbohrungen gelenkt werden. Es können aber auch mehrere Strahlen bzw. mehrere Analysatoren verwendet werden, so daß eine gleichzeitige Aufnahme von Spektren mit mehreren Reaktoren möglich ist. Es kann aber ebenso der Block mit den Reaktoren mittels Bewegungseinrichtungen, beispielsweise Schrittmotoren, so bewegt werden, daß alle Küvettenbohrungen nacheinander in den Strahlengang des

Spektrometers gebracht werden. Als Werkstoffe für Block und Abstandshalter eignen sich vorzugsweise die gängigen, dem Fachmann geläufigen korrosionsbeständigen metallischen Werkstoffe, besonders Aluminium oder Stahl, vorzugsweise rost- und/oder säure- und/oder hochtemperaturbeständig.

Eine weitere Ausgestaltung der erfindungsgemäßen Vorrichtung, die sich besonders für die homogene Katalyse eignet, ist dadurch gekennzeichnet, daß bei mindestens einem Reaktor mit einem Volumen, das bevorzugt kleiner als 200 μ l ist, ein ATR-Kristall (Attenuated Total Reflection Spectroscopy, bevorzugt konisch spitz, bevorzugt aus ZnSe oder aus KSR5 oder aus Diamant) den spektroskopischen Kontakt zum Reaktionsgemisch bei unterschiedlichen Lösungsmitteln und Reaktionsbedingungen und Drücken bis 200 bar ermöglicht. In diesem Fall wird der Analysestrahl auf den ATR-Kristall fokussiert.

Die Vorteile des erfindungsgemäßen Verfahrens und der erfindungsgemäßen Vorrichtung liegen im wesentlichen darin, daß eine Vielzahl von Reaktionen unter praktisch identischen Bedingungen und mit vergleichsweise geringen Substanz- und Probenmengen schnell, kostengünstig und reproduzierbar durchgeführt und dabei gleichzeitig spektroskopisch untersucht werden kann. Sie bietet damit die Möglichkeit, die im Zusammenhang mit der kombinatorischen Chemie diskutierten Möglichkeiten (K. Burgess et al., Ang. Chem. 1996, 108, 2, 192, durch Bezugnahme mit in die Anmeldung integriert) für ein industrielles Katalysatorscreening einzusetzen. Durch die Wahl identischer Proben und unterschiedlicher sonstiger Reaktionsbedingungen wie Temperatur, Druck, Eduktzusammensetzung kann eine parallele Reaktionsoptimierung durchgeführt werden.

Zur Analyse der gewonnenen Daten wird vorteilhafterweise eine Datenmatrix dergestalt aufgestellt, daß alle wählbaren und dokumentierbaren Reaktionsbedingungen (Edukt-Partialdrücke, Eduktzusammensetzung, Temperatur, Durchfluß bzw. Durchflußrate, Gesamtdruck,

Probenzusammensetzung, Probengitterparameter und alle Stützstellen der Spektren) nach Reaktionsbedingungen, d.h. je Reaktor, als Spalten der Matrix dargestellt werden. Diese Matrix kann einer Faktorenanalyse (E.R. Malinowski et. al., Factor Analysis in Chemistry, Wiley, New York, 1980, durch Bezugnahme mit in die Anmeldung integriert) unterzogen werden, indem man die Covarianzmatrix, die Eigenwerte, die abstrakten Eigenvektoren, die Loadings sowie die Koeffizienten der mehrdimensionalen Regression berechnet und bevorzugt als Dateien ausgibt. Es kann auch eine (Vor-)Normalisierung der Daten durch den Mittelwert "0" und Standardabweichungen "1" gewählt werden, wodurch Grundlinien- oder Absolutbetrageffekte vermieden werden können. Dies erlaubt die Vorhersage verschiedener Größen aus Eichdatensätzen (wie z.B. quantitative CO₂-Anteile bei verschiedenen Temperaturen), die Bestimmung der Abhängigkeit von Parametern in Spektralbereichen zur Optimierung der Analytik, die Generierung unterschiedlicher Distanzmatrizen aus den Ausgangsdaten (beispielsweise die Ähnlichkeit von Katalysatoren bezüglich der ausgewählten Größen und Eigenschaften) und das direkte Rückkoppeln der Katalysatorzusammensetzung auf einen Syntheselaborroboter, der einen Satz neuer Katalysatorproben mischt, und durch Sintern bzw. Kalzinieren auf einer Roboterstraße "selbständig" synthetisiert.

Im folgenden wird eine Ausführungsform des erfindungsgemäßen Verfahrens und eine Ausgestaltung der erfindungsgemäßen Vorrichtung anhand der Figuren 1 bis 2 näher erläutert, ohne daß dadurch beabsichtigt ist, die Erfindung in irgendeiner Weise zu beschränken.

Es zeigt

- Fig. 1 eine schematische Darstellung der erfindungsgemäßen Vorrichtung 1 im Strahlengang eines spektroskopischen Analysators;
- Fig. 2 einen einzelnen Reaktor 2 aus der erfindungsgemäßen Vorrichtung 1 in seitlicher Schnittansicht.

Eine Vorrichtung 1 zur Untersuchung von chemischen Reaktionen besteht im wesentlichen aus einer blockförmigen Anordnung 3 von miniaturisierten Reaktoren 2. Die blockförmige Anordnung 3 ist in der Weise ausgeführt, daß die Reaktoren 2 in einem quaderförmigen Metallblock 4, der eine Vorderseite 6 und eine Rückseite 7 aufweist, in der Form von Bohrungen eingearbeitet sind. Die Reaktoren 2 sind in die Vorderseite 6 des quaderförmigen Metallblocks 4 eingesenkt und in einem rechteckigem Muster angeordnet. Sie sind zum Zuführen der Edukte mit Bohrungen 5 verbunden. In die Reaktoren 2 sind Katalysatoren 8 eingebracht. Auf die Vorderseite 6 ist als Abstandshalter eine Distanzplatte 9 aufgebracht, in der sich die Reaktoren 2 als Bohrungen fortsetzen. Von diesen führen weitere Bohrungen 10, die der Ableitung der Reaktionsprodukte dienen, zu einer Küvettenbohrung 11. Auf der Rückseite 7 ist als weiterer Abstandshalter eine Distanzplatte 12 angeordnet. Die Küvettenbohrung 11 setzt sich durch den Metallblock 4 hindurch bis durch die Distanzplatte 12 hindurch fort. Sie ist an den freien Oberflächen der Distanzplatten mit transparenten Fenstern 13 verschlossen und dient der Ableitung der Reaktionsprodukte und gleichzeitig als Raum für deren spektroskopische Analyse mittels eines IR Strahls 14. Die Reaktionsprodukte werden, vom Reaktor 2 kommend, entsprechend den eingezeichneten Pfeilen durch die Bohrungen 10,11 geleitet. Vom Ende der Küvettenbohrung 11 in der Distanzplatte 12 werden sie über Bohrungen 15 abgeleitet. In der Nähe der Reaktoren 2 sind Heizelemente 17 und Thermoelemente 18 in den Metallblock 4 eingebracht. Die blockförmige Anordnung 3 ist durch Schrittmotoren 16 in beide Raumrichtungen senkrecht zum IR-Strahl 14 bewegbar. Dadurch kann

jede zu einem der Reaktoren 2 gehörige Küvettenbohrung 11 in den IR-Strahl bewegt werden. Die Analyse des IR-Strahls erfolgt durch Aufnahme des Interferogramms mittels Interferometer 20 und Detektor 19, die nahe den transparenten Fenstern 13 angeordnet sind.

Im folgenden wird ein Versuchsbeispiel mit einem bekannten Katalysator beschrieben.

In der erfindungsgemäßen Vorrichtung wurden in den Reaktoren des Reaktorblockes unterschiedliche Feststoffe mit einem Gemisch aus 30,2 Vol.-% Propylen 2.5, 15,2 Vol.-% Sauerstoff 4.5, Rest Stickstoff 5.0 beströmt. Einer der Reaktoren enthielt eine kleine Menge (5 mg) eines bekannten, industriellen Katalysators für die Oxidation von Propylen zu Acrolein. Vollautomatisch wurden die IR-Spektren aller Reaktionsgase bei unterschiedlichen Temperaturen aufgenommen. Fig.3 zeigt das Spektrum des Reaktionsgases des Reaktors, der den bekannten Katalysator enthielt bei 400 und 450 °C: Bei 400 °C kann bereits das Produkt (Acrolein aus Sauerstoff und Propylen) nachgewiesen werden. Es entstand allerdings noch viel Kohlendioxid. Bei 450 °C wurde kein Kohlendioxid mehr festgestellt, die Ausbeute an Produkt hatte zugenommen. (Die leichte negative Bande entstand durch Referenzierung und gibt die Grundliniengenauigkeit in diesem Experiment wieder.)

Somit wurde gezeigt, daß eine Katalysatoraktivität für eine spezielle Reaktion vollautomatisch nachgewiesen und optimiert werden kann.

Patentansprüche

1. Verfahren zur Untersuchung von chemischen Reaktionen in Gegenwart von potentiell katalytischen Substanzen, bei dem man die Reaktionen parallel in Reaktoren durchführt, dadurch gekennzeichnet, daß man die Reaktionen in miniaturisierten Reaktoren durchführt und das Reaktionsgemisch während der Reaktionszeit nach Art und Menge analysiert.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man die Reaktionsedukte laufend den Reaktoren zuführt und die Produkte laufend aus den Reaktoren abführt.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß man die Reaktionen bei unterschiedlichen Temperaturen durchführt, vorzugsweise bei Temperaturen aus dem Bereich von Raumtemperatur bis einschließlich 600°C oder bei unterschiedlichen Drücken, vorzugsweise bei Absolutdrücken von 10^{-3} bis 10^3 bar, besonders bevorzugt von 10^{-2} bis 200 bar.
4. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die potentiellen Katalysatoren heterogene oder homogene Katalysatoren sind.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man pro Reaktor eine Katalysatormenge < 10 mg, bevorzugt < 1 mg verwendet.
6. Verfahren nach einem oder mehreren der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß man das Reaktionsgemisch oder die Reaktionsprodukte spektroskopisch nach Art und Menge der Bestandteile

analysiert, vorzugsweise mit IR-Spektroskopie.

7. Verfahren nach einem oder mehreren der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß man die Reaktionen in mehr als 20, bevorzugt mehr als 40, besonders bevorzugt mehr als 100 Reaktoren durchführt.
8. Verfahren nach einem oder mehreren der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß man Reaktionen der homogenen oder heterogenen Katalyse mit flüssigen oder gasförmigen Edukten oder Produkten untersucht.
9. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß man die spektroskopische Analyse an allen Reaktoren gleichzeitig durchführt indem man eine entsprechende Zahl von Analysatoren einsetzt, oder daß man die spektroskopische Analyse an den Reaktoren nacheinander durchführt, in dem man einen Analysestrahl, mittels einer Ablenkvorrichtung nacheinander auf die einzelnen Reaktoren richtet oder indem man die Reaktoren mittels einer Bewegungseinrichtung nacheinander in den Analysestrahl bringt.
10. Verfahren nach einem oder mehreren der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß man Edukte verwendet, die mindestens teilweise mit Isotopen markiert sind, bevorzugt mit Deuterium oder schweren Sauerstoff oder schweren Kohlenstoff.
11. Verfahren nach einem oder mehreren der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß einzelnen oder zu Gruppen zusammengefaßten Reaktoren unterschiedliche Eduktgemische zugeführt werden.
12. Vorrichtung, insbesondere zur Durchführung des Verfahrens gemäß

Anspruch 1, wobei die Vorrichtung mehrere, parallel geschaltete Reaktoren aufweist, die mit Zu- und Ableitungen versehen sind, dadurch gekennzeichnet, daß die Reaktoren miniaturisiert sind, bei einem Volumen aus dem Bereich von $0,001 \text{ cm}^3$ bis 1 cm^3 .

13. Vorrichtung nach Anspruch 12, dadurch gekennzeichnet, daß die Reaktoren in der Form eines Blocks angeordnet sind, vorzugsweise rechteckig oder quadratisch.
14. Vorrichtung nach Anspruch 12 oder 13, dadurch gekennzeichnet, daß die Zuleitungen oder die Ableitungen oder die Reaktoren mindestens teilweise für Analysestrahlung, vorzugsweise für Infrarot-, Laser- oder UV-Licht transparent sind.
15. Vorrichtung nach einem oder mehreren der Ansprüche 12 bis 14, dadurch gekennzeichnet, daß die Reaktoren in einem quaderförmigen Metallblock angeordnet sind, der mit Heizelementen und/oder Temperaturmeßstellen ausgerüstet ist.
16. Vorrichtung nach einem oder mehreren der Ansprüche 12 bis 15, dadurch gekennzeichnet, daß die Vorrichtung mit Bewegungseinrichtungen versehen ist, vorzugsweise mit Schrittmotoren.
17. Vorrichtung nach einem oder mehreren der Ansprüche 12 bis 16, dadurch gekennzeichnet, daß die Vorrichtung mehr als 20, bevorzugt mehr als 40, besonders bevorzugt mehr als 100, ganz besonders bevorzugt mehr als 200 Reaktoren aufweist.
18. Vorrichtung nach einem oder mehreren der Ansprüche 12 bis 17, dadurch gekennzeichnet, daß mindestens ein Reaktor mit einem ATR-

Kristall ausgerüstet ist, der einen spektroskopischen Kontakt zum Reaktionsgemisch ermöglicht.

19. Vorrichtung nach Anspruch 15, dadurch gekennzeichnet, daß die Reaktoren in einer Ebene parallel zu einer Oberfläche des Metallblockes angeordnet sind, daß die Zu- oder Ableitungen mindestens abschnittsweise senkrecht zu dieser Ebene gelegt sind, daß auf der Oberfläche eine Abstandshalter angebracht ist, der Bohrungen aufweist, durch die die Reaktoren oder die Ableitungen verlängerbar sind, daß der Metallblock und die Abstandshalter Küvettenbohrungen aufweisen und daß auf der Abstandsplatte für Analysenstrahlung transparente Fenster angebracht sind, die die Küvettenbohrungen gegen die Umgebung verschließen.
20. Vorrichtung nach einem oder mehreren der Ansprüche 12 bis 19, dadurch gekennzeichnet, daß die Reaktoren Katalysatoren ebthalten, bevorzugt mit einem Gewicht kleiner als 10 mg pro Reaktor, besonders bevorzugt mit einem Gewicht kleiner als 1 mg pro Reaktor.

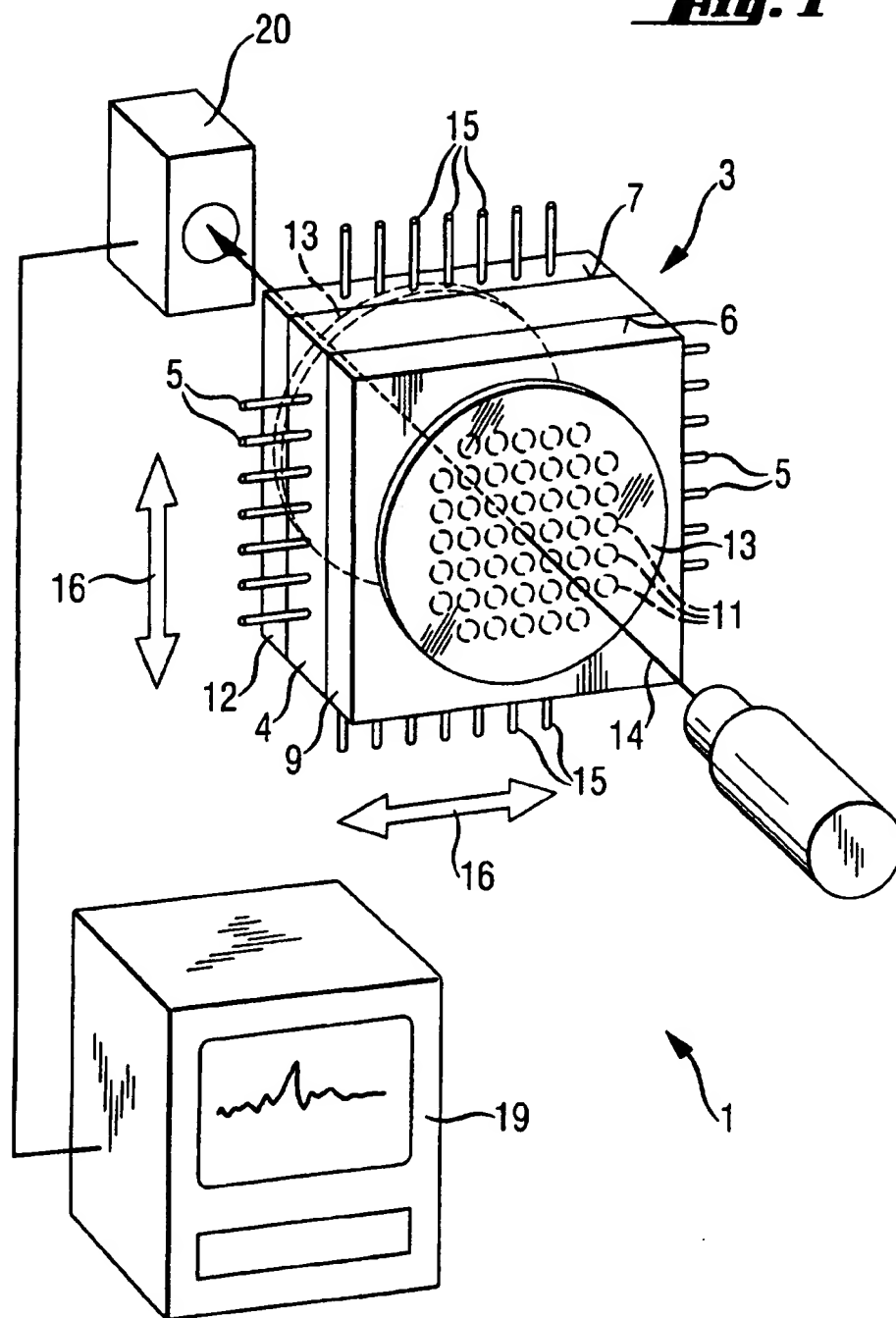
Fig. 1

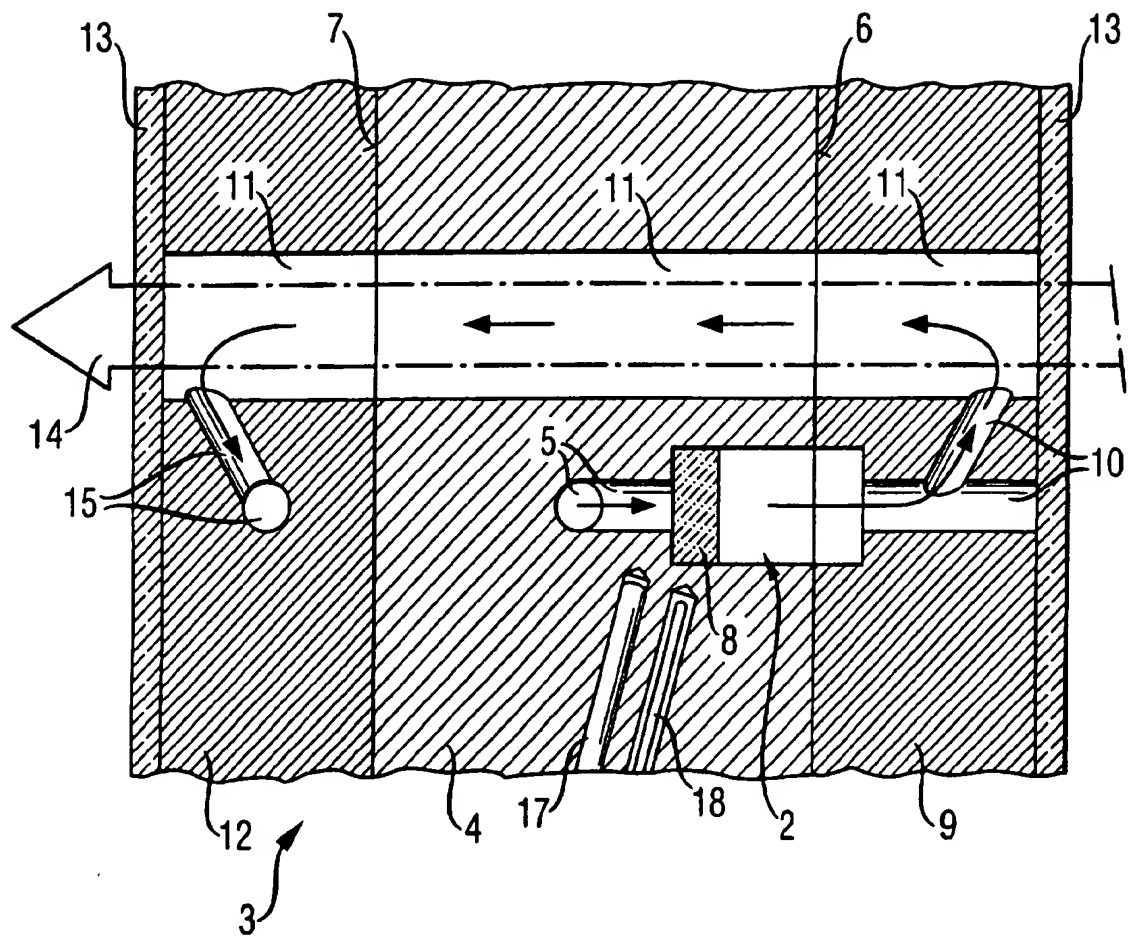
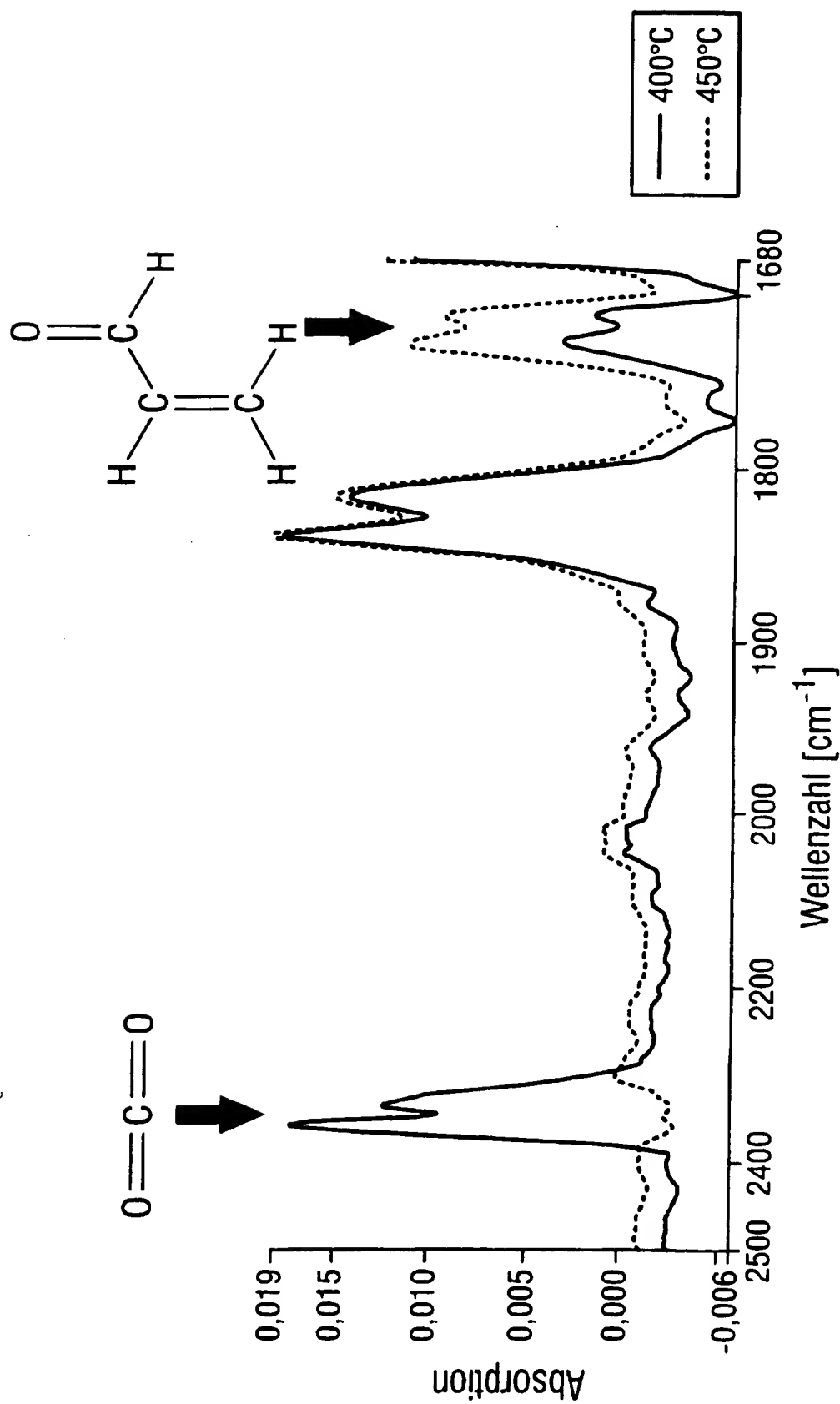
Fig. 2

Fig. 3: Screening und Optimierung eines Katalysators
durch IR-Gasanalytik online im parallelen Reaktor



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 099 923 A (MILBERGER) 11 July 1978 see abstract see column 3, line 36 - line 63; figure 1 ---	1
Y	US 3 431 077 A (JOSEPH D. DANFORTH) 4 March 1969 see column 1, line 8 - line 21 see column 4, line 35 - line 46; figure 1 ---	1
A	US 5 266 270 A (AJOT ET AL.) 30 November 1993 see abstract see column 1, line 12 - line 37; figure 1 -----	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4099923 A	11-07-78	NONE	
US 3431077 A	04-03-69	NONE	
US 5266270 A	30-11-93	FR 2583519 A	19-12-86
		DE 3689944 D	11-08-94
		DE 3689944 T	08-12-94
		EP 0206905 A	30-12-86
		US 4988626 A	29-01-91

INTERNATIONALER RECHERCHENBERICHT

Interne Aktenzeichen

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A. KLASSTIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

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Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

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C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	US 4 099 923 A (MILBERGER) 11. Juli 1978 siehe Zusammenfassung siehe Spalte 3, Zeile 36 - Zeile 63; Abbildung 1	1
Y	US 3 431 077 A (JOSEPH D. DANFORTH) 4. März 1969 siehe Spalte 1, Zeile 8 - Zeile 21 siehe Spalte 4, Zeile 35 - Zeile 46; Abbildung 1	1
A	US 5 266 270 A (AJOT ET AL.) 30. November 1993 siehe Zusammenfassung siehe Spalte 1, Zeile 12 - Zeile 37; Abbildung 1	1-3

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Im Recherchenbericht angeführtes Patentedokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
US 4099923 A	11-07-78	KEINE	
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In der Festkörperphysik unterliegen Übergänge zwischen verschiedenen elektronischen Zuständen den durch die /Kristallsymmetrie bedingten Verboten. Die /Bloch-Funktionen haben infolge der Kristallsymmetrie bestimmte Translationseigenschaften, die, zusammen mit /Symmetrieeigenschaften des die Übergänge bewirkenden Störpotentials, das notwendige Verschwinden gewisser /Übergangsmatrixelemente zur Folge haben.

Die Auswahlregeln für solche verbotenen Übergänge lassen sich mit gruppentheoretischen Methoden über die /Charaktere gewinnen (/Darstellung von Gruppen). Besonders wichtig sind die Auswahlregeln für optische Übergänge.

Für die Reaktionen der Elementarteilchenphysik gelten entsprechende Auswahlregeln, z.B. die Erhaltung der Ladung oder der Baryonenzahl. Dagegen ist die Stringenz bei schwachen Wechselwirkungen keine Erhaltungsgröße.

Ausweichprobleme, Stabilitätsprobleme, Probleme aus der /Elastizitätstheorie, bei denen nach Überschreiten kritischer Lastwerte bei der Verformung von Bauteilen (z.B. Stäben, Scheiben, Platten, Schalen) Instabilitätsvorgänge wie Knicken, Beulen, Kippen, Stülpen oder Biegedrillknicken einsetzen. Die Berechnung der kritischen Lastwerte führt auf Eigenwertprobleme (/Eigenwerte).

ausw. ... den das Ausgleichen einer statischen oder dynamischen Unwucht bei einem /Kreisel, meist einem Rad, durch Anbringen seiner Gewichte an geeigneten Stellen. Als statische Unwucht bezeichnet man den Fall, daß die zum größten Hauptträgheitsmoment (/Trägheitsmoment) gehörende Trägheitsachse durch die Rotationsachse des Kreisels steht. Wird die Rotationsachse festgehalten, so macht sich zu bei einer Drehung des Kreisels durch Kräfte auf die Lager bemerkbar. Diese Unwucht ist auch dafür verantwortlich, daß sich ein möglichst reibungsfrei horizontal aufgelagerter Kreisel aufgrund der Erdanziehung immer mit derselben Stelle nach unten einstellt. Im Gegensatz dazu verursacht die dynamische Unwucht nur Kräfte auf die Lager. Sie tritt auf, wenn die Hauptträgheitsachsen die Rotationsachse schneiden, aber nicht mit ihr zusammenfallen. Der Schwerpunkt liegt in diesem Fall auf der Rotationsachse.

Auswurftheorie /Ejektionstheorie der Spiralstruktur.

Autobatterie / Starterbatterie, /Bleibakkumulator, /Akkumulator.

Autofluoreszenz, Fähigkeit einiger Stoffe zur /Fluoreszenz bei Lichteinstrahlung, ohne daß zusätzlich Fluorochrome eingebracht werden müssen. Autofluoreszierende Materialien werden in der /Fluoreszenzmikroskopie gern als Referenzproben eingesetzt, da diese oft ohne aufwendige Präparation hergestellt werden können. Im Gegensatz zur Autofluoreszenz einiger Materialien müssen bei der großen Mehrzahl von Stoffen, die nicht selbst zur Fluoreszenz fähig sind, spezielle fluoreszierende Farbstoffe (oft toxisch) zugefügt werden. **Autoguides,** Hilfsmittel an größeren Teleskopen, das die automatische Nachführung verbessert. Bei einem Autoguide wird das Bild eines geeigneten Leuchters in der Umgebung des zu untersuchenden kosmischen Objekts computergesteuert innerhalb eines Kreises von etwa einer Bogensekunde oder weniger gehalten. Wandert der Stern, etwa durch Rastungenauigkeiten der Nachführung, aus diesem Gebiet heraus, wird das Teleskop entsprechend gegengesteuert.

Autoionisation, Prozeß, der bei der Anregung von Atomen oder Molekülen auftreten kann, wenn der angeregte Zustand energetisch über dem Ionisationspotential liegt. In Molekülen ist dies möglich, wenn ein angeregter Rotations-Schwingungs-Zustand des neutralen Moleküls höher liegt als ein solcher Zustand des Molekülions. In Atomen kann die Anregungsenergie eines inneren Schalelektrons ausreichen, um ein Elektron einer weiter außen liegenden Schale über das Ionisationspotential anzuheben; (z.B. /Auger-Effekt).

Autokatalyse, physikalisch-chemischer Prozeß, bei dem der Katalysator ein Produkt der von ihm selbst katalysierten chemischen Umwandlung ist. Dadurch kommt es zu einem sehr schnellen Anstieg der Produktkonzentration. Autokatalyse gibt es nicht nur in der unbelebten Welt (z.B. Beschleunigung der Titration von Oxalsäure mit Kaliumpermanganat durch die bei der Reaktion entstehenden Mn^{2+} Ionen), sondern auch in lebenden Systemen (/Enzyme).

Autoklav, aufheizbares, druckfestes Gefäß, das luftdicht abgeschlossen werden kann und zur Durchführung chemischer Reaktionen (z.B. Polymerisationen) bei hohen Drücken oder zur Sterilisation medizinischer Geräte oder Dosenkonserven mit Hilfe von überhitztem Wasserdampf verwendet wird. Bei der Sterilisation wird Wasserdampf mit einem Überdruck von $1-2 \cdot 10^5$ Pascal und einer Dampftemperatur von $120-134^\circ\text{C}$ zur Abtötung von Mikroorganismen verwendet (/Sterilisationsmethoden).

Autokollimation, optisches Verfahren, um Fernrohre (z.B. in Spektrometern) schnell und genau auf unendlich einzustellen. Über

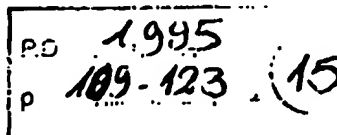
Translation of the entry "Autoklav" in R1

Autoclave, heatable, pressure resistant vessel which may be closed airtight and used for the performance of chemical reactions (e.g. polymerizations) at elevated pressures or for sterilisation of medical devices or canned food by means of overheated steam. In the sterilisation steam with an overpressure of $1-2 \times 10^5$ Pascal and a vapour temperature of $120-134^\circ\text{C}$ for killing micro organisms are used (sterilisation methods).

XP-000925640

Modular Concept for Miniature Chemical Systems

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Summary

Miniaturised chemical systems comprise components for fluid manipulation (channels, pumps, valves etc.), (bio)chemical reaction and analysis. We propose a generic concept consisting of a so-called Mixed Circuit Board (MCB) containing both the fluidic channels and electrical circuitry as well as the silicon-based modules. The modules have a standardized connection to the MCB both for fluids as for electrical signals. In- and output modules have connections with capillaries used for liquid chromatography, ensuring the compatibility with this separation technique. The MCB itself consists either of glass-bonded silicon with anisotropically etched channels, but can ultimately be made as plastic component with use of moulding techniques. A number of system components such as a micropump, a capillary connector, a flow sensor, a micromixer (reactor) and a microfilter will be presented. An example of an electrochemical microreactor (microtitrator) will be given, and it will be shown how incorporation of this microreactor in a Micro Total Analysis System (μ TAS) improves its performance. Finally a potential future realisation of a more complicated system, a parallel multisystem for chemical processparameter optimisation, will be evaluated.

Zusammenfassung

Miniaturisierte chemische Systeme bestehen aus verschiedenartigen Komponenten zur 'Kontrolle' von Flüssigkeiten (Kanäle, Pumpen, Ventile, etc.), zur Erzeugung von (bio)chemischen Reaktionen und zur Analyse. Es wird ein allgemeines Konzept für ein derartiges System vorgeschlagen, das aus einem sogenannten Mixed Circuit Board (MCB) besteht, und welches sowohl die eigentlichen Flußkanäle und die elektrische Schaltung als auch die auf Siliziumtechnologie basierenden Module beinhaltet. Diese Module besitzen eine standardisierte Verbindung zum MCB, und zwar sowohl für die Flüssigkeiten als auch für die elektrischen Signale. Die Ein- und Ausgangsmodule weisen Verbindungen zu Kapillaren auf, die zur Flüssigkeitschromatographie verwendet werden, und stellen damit die Kompatibilität zu dieser Trenntechnik sicher. Für das MCB selbst verwendet man üblicherweise glasgebundenes Silizium mit anisotrop geätzten Kanälen, es kann letztendlich allerdings auch aus Plastikkomponenten bestehen, die mittels spezieller Formtechniken erzeugt werden. Ein Teil dieser Systemkomponenten, wie zum Beispiel Mikropumpe, Kapillarverbindung, Flussensor, Mikroreaktor und Mikrofilter, werden vorgestellt. Weiterhin wird ein Beispiel eines elektrochemischen Mikroreaktors (Mikrotitrator) präsentiert, und es wird gezeigt, wie die Einbindung dieses Mikroreaktors in ein 'Totales-Mikro-Analyse-System' (Micro Total Analysis System = μ TAS) die Funktionsweise des gesamten Systems verbessert. Zuletzt wird eine mögliche zukünftige Realisierung eines komplizierteren und komplexeren Systems - ein parallel arbeitendes Mehr-Komponenten-System zur Optimierung chemischer Prozeßparameter - diskutiert.

1. Introduction

During the past few decades a large variety of chemical microsensors has been developed. A large amount of sensor principles such as optical, electrochemical, mass-sensitive and calorimetric have been developed [1]. However, few of these sensors have made the way to the market. One of the main reasons for this was the inherent limitation of chemical sensor performance caused by sensor drift and loss of selectivity and sensitivity. For this reason, actuators were added which enabled calibration of the sensor. Thanks to revolutionary developments in silicon microtechnology, in the last decade many so-called fluid-handling elements have been developed. Using these elements, complete micro-analysis systems could be built. One of the problems encountered with such systems, however, is that due to their high complexity it is virtually impossible to develop and fabricate all necessary components alone. For this reason we have developed a generic hybrid concept, a "Micro Fluidic System" (MFS) enabling the composition of a complex analysis system by integrating different components on one "motherboard" [2].

A logical further step in the realization of microsystems is the addition of some sort of micro reaction chamber to the system. Such a chamber may be used to simply mix two chemical reagents [3], or carry out a thermally induced chemical reaction in liquid [4] or gas phase (using a catalyst) [5]. The whole process of integration is illustrated in fig. 1.

In this paper the MFS concept, as well as several components used in it will be described. Besides, an example of a electrochemical sensor-actuator system (microtitrator) will be given. Because of some shortcomings of this system, it will be shown how incorporation of this microreactor in a Micro

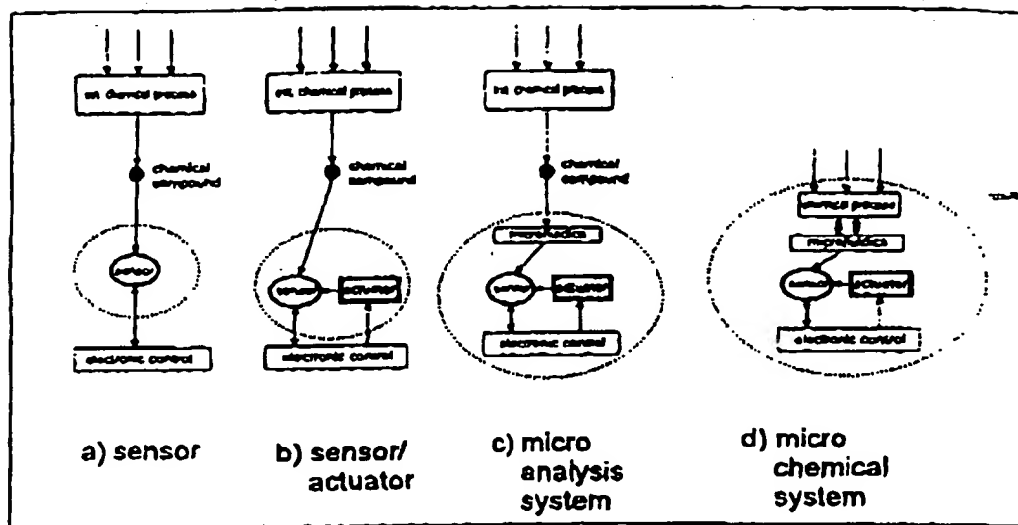


Fig. 1 Process of integration of sensors, actuators, fluidics and reactors into a micro chemical system.

Total Analysis System (μ TAS) improves its performance. Finally some potential future realisations of more complicated systems, such as a parallel multisystem for chemical process-parameter optimisation, will be evaluated.

2. Micro Fluid System (MFS) Concept

For the integration of components for fluid-handling into a system, several approaches have been proposed. Van der Schoot et al. [6] proposed a vertical, stackwise arrangement of components which has the advantage of efficient use of surface area but the disadvantage of being rather inflexible. An alternative was presented by Fiehn et al. [7], who presented a Fluidic ISFET-Microsystem (FIM) based on a planar integrated system. The main disadvantage of this system is that a whole processed glass-bonded silicon wafer is used as system substrate. Recently, an alternative was presented in

which the components are at least partly, reversibly mounted in a way perpendicular to the substrate [8]. In the latter system, which uses a silicon bonding for hermeticity, the advantage is that each component can be replaced. The disadvantage is that the fabrication of the system is not easily automated.

The Micro Fluidic System (MFS) we propose is composed of a so-called Mixed Circuit Board (MCB) containing the fluid channels as well as the electronic circuitry in combination with the silicon-based fluidic components (modules). These modules have a standardised connection to the planar MCB both for fluids and electrical signals. The MCB consists of a glass-bonded silicon backplate in a first stage, whereas in the second stage (laminated) plastics are used (see fig.2). In fig. 3 an example is given of how the electrical and mechanical layout of such a microanalysis system looks like.

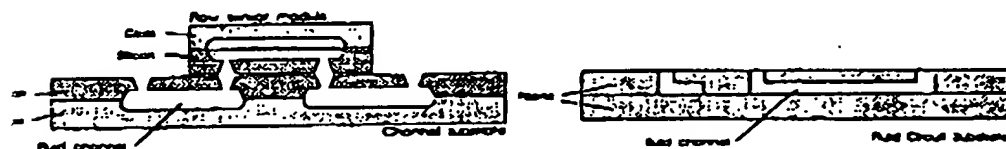


Fig. 2 Flow sensor module on Si-glass bonded substrate (left) and plastic Mixed Circuit Board (right).

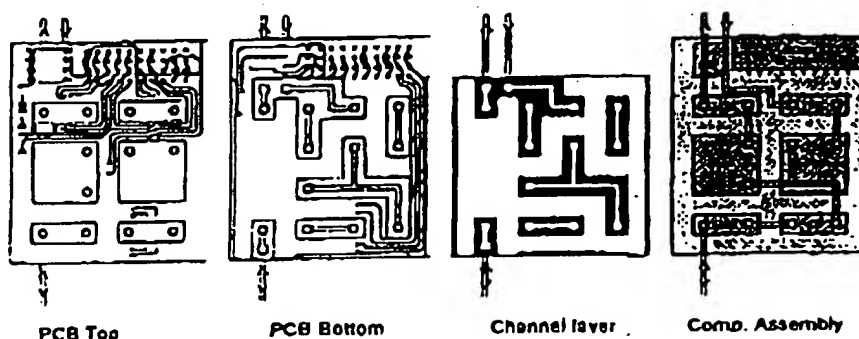


Fig. 3 Schematics of floorplan with mixed electrical and fluid connections.

For the realisation of Micro Fluidic Systems (MFS) a wide variety of components is needed. Many of them, like pumps, flow-sensors and filters, were already developed at MESA [9]. For integration in the MFS new designs have been made of a number of components that made them compatible with mentioned concept. In Fig. 4 examples are shown of a flow sensor, a resistor, a filter/mixer module, a micropump, and a microvalve specially designed for integration in MFS.

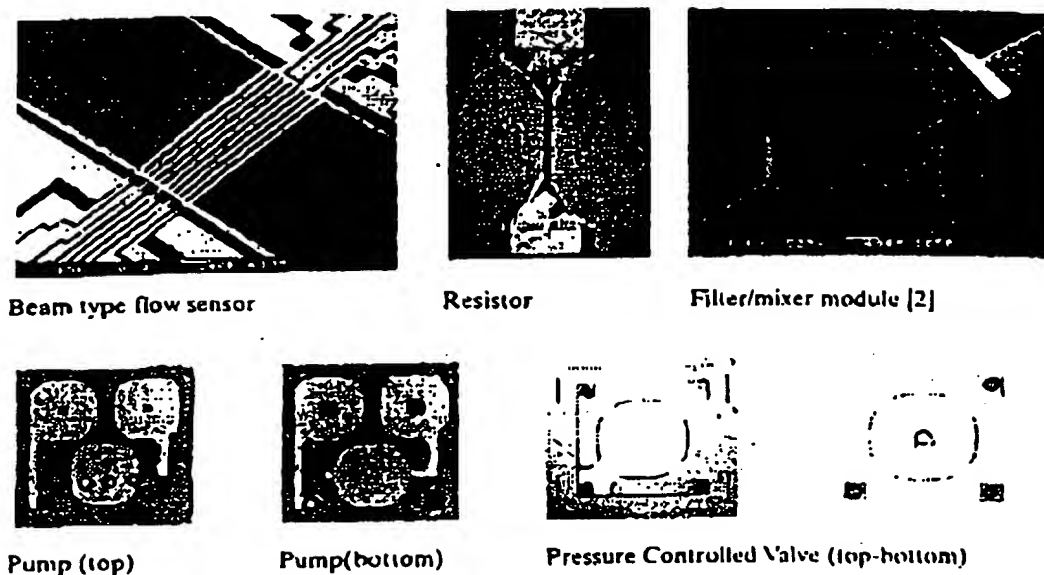


Fig. 4 Photographs of a number of different components for the Micro Fluidic System (MFS).

3. Coulometric Microtitrator

In earlier studies, the development of a coulometric acid/base titrator has been described [12,13]. This structure consists of an electrochemical actuator combined with an ISFET pH-sensor (see fig. 5).

With this sensor-actuator device fast titrations can be carried out, and the titration time t_{end} is directly related to the acid/base concentration to be determined via the formula:

$$\frac{\partial \sqrt{t_{\text{end}}}}{\partial C_{\text{acid}}} = \frac{F \sqrt{\pi D_{\text{acid}}}}{2 j_c}, \quad (1)$$

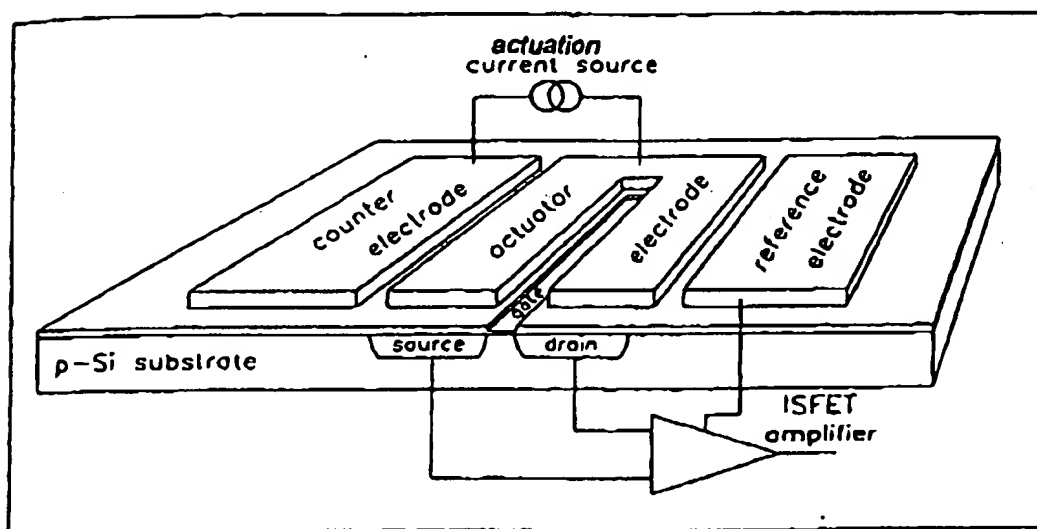


Fig. 5 Basic elements of the coulometric sensor-actuator device.

with j_c is the cathodic current density through the actuator, C_{acid} and D_{acid} respectively the concentration and diffusion coefficient of the acid and F is Faraday constant. A typical plot of the square root of t_{end} vs. acid concentrations of acetic and nitric acid is shown in figure 6.

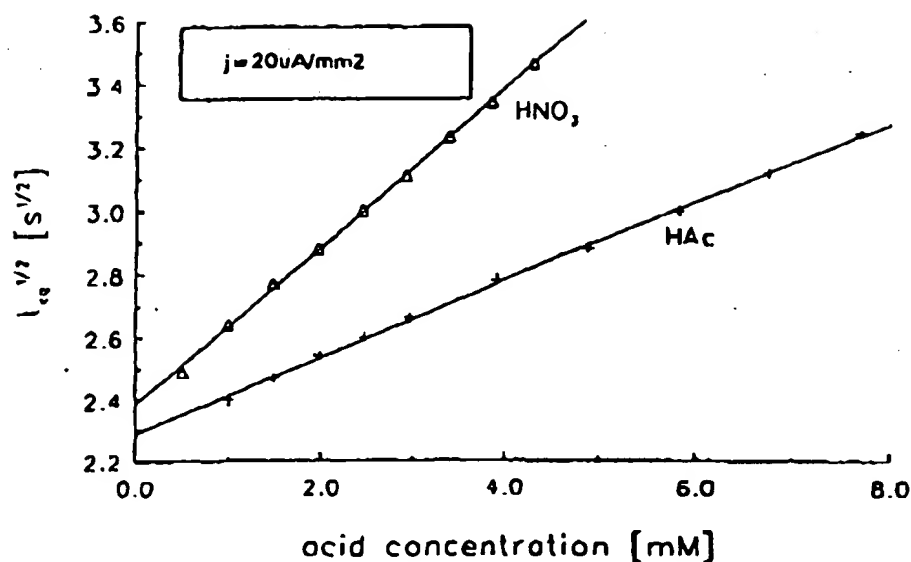


Fig. 6 Square root of t_{end} as a function of both HAc and HNO₃ concentrations.

In practice, it appears that the coulometric actuator device, if operated as such, shows some disadvantages. First of all, there is no linear relation between titration end point and the required concentration. Secondly, the proper functioning of the device relies on the presence of only one type of mass transport: diffusion. Effects of migration may strongly influence the measurement, and to overcome this an excess concentration of supporting electrolyte is needed. Finally, as shown in fig. 6, the operational range is limited to a maximum of approximately 10 mM, caused by limitations in the current density. This upper limit turns out to be problematic with respect to the much higher total acid concentrations in several food products, such as fruit juice or wine (50 to 150 mM). The problems mentioned above can be overcome by incorporation of the microtitrator in a Micro Total Analysis System (μ TAS).

As a start, let us consider the sensor-actuator device in differential mode to be placed in a small-volume reaction chamber, as schematically shown in figure 7. The height h of the reaction chamber is chosen small (typically 25 μm) with respect to the mean diffusion layer thickness after a few seconds of titrant generation (typically 100 to 500 μm). In addition, the actuator area A is chosen large (e.g. 1 to 5 mm^2) with respect to the mean diffusion layer thickness. Consequently, a homogeneous coulometric titration can be considered to take place in the volume formed by $A \cdot h$. The slope of the curve, resulting from a series of measurements in different acid concentrations, C_{acid} , can now be expressed as

$$\frac{\partial t_{\text{end}}}{\partial C_{\text{acid}}} = \frac{FAh}{I_c} \quad (2)$$

with I_c is the current through the actuator. When comparing (1) with (2), it is clear that in the latter equation the diffusion coefficient is absent: regardless of any difference in the diffusion coefficient, the time to reach the end point t_{end} in the titration curve will, for a constant current I_c , depend only on the acid concentration (expressed in its corresponding normality). This is an important advantage over the former operation principle: that of free diffusion. It is also clear from (2) that the relation between the acid concentration and t_{end} is linear, which may simplify subsequent signal processing.

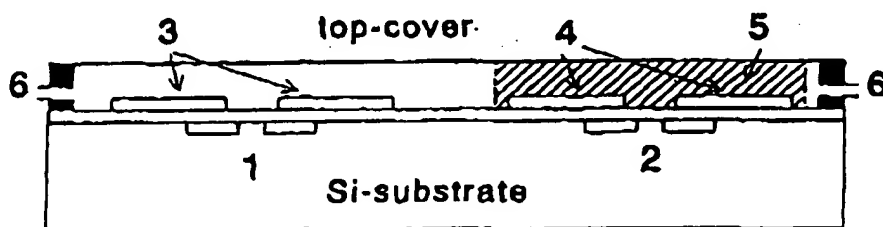


Fig. 7 Reaction chamber with (1) reference ISFET, (2) indicator ISFET, (3) pseudo-ref. electrode, (4) actuator, (5) titration volume and (6) spacer with inlet and outlet.

A. van den Berg

Because lateral mass transport still would influence the measuring result, convection must be avoided, which is very easy in the small-volume reaction chamber after the valve controlling the inlet flow is closed: the sample in the reaction chamber will be at rest immediately.

Considering migration, the second undesirable means of mass transport, another advantage of μ TAS comes in view: the possibility to add supporting electrolyte. Both the proper control of the titrant-generating actuator current and the avoidance of migration requires a lower limit for the ion strength of the sample. With μ TAS, a very small volume of a high concentration of neutral supporting electrolyte can be added and mixed with the analyte in a mixing chamber, thereby hardly changing the concentration of the acid. Finally, the injection and mixing of moderate volumes of supporting electrolyte can be used to deliberately dilute the sample in order to be able to measure high acid (or base) concentrations, e.g. in fruit juices.

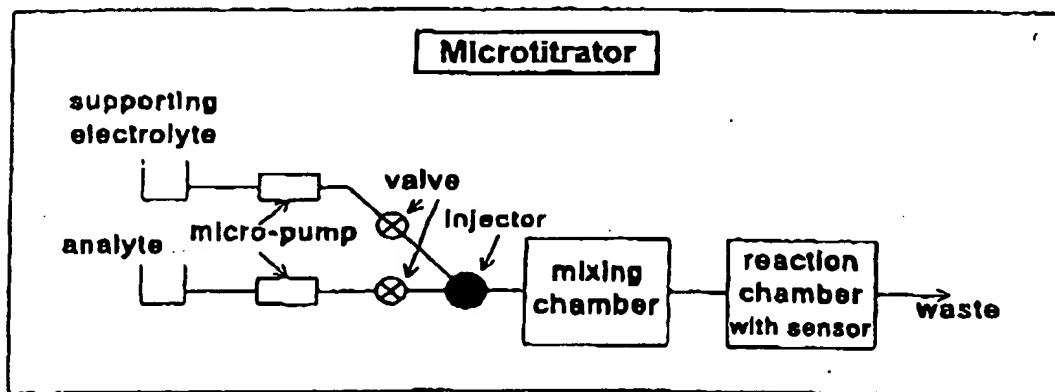


Fig. 8 The proposed μ TAS for improved coulometric sensor-actuator performance.

The μ TAS thus proposed, including subsystems, is schematically shown in figure 8. In reality the mixing and reaction chamber might be one chamber only. Also, the micro-pump itself might function as a valve.

4. Micro Chemical Reactor Array

Monocrystalline silicon is particularly suited for the realization of anisotropically etched micro chambers or reactors, closed at one side by a thin membrane. A thin film heater can be deposited on this membrane enabling the most straightforward way of heating the reactor volume, both for liquids as gases [14,15]. Furthermore the microreactor is easily combined with a thin film catalyst (Pt) such as used for catalytic gas sensors [5] and can be covered by a glass cover, allowing optical excitation. Finally, the Pyrex-silicon sealing is tight enough to make experiments under high pressure (up to 200 bar [16]) possible (see fig. 9).

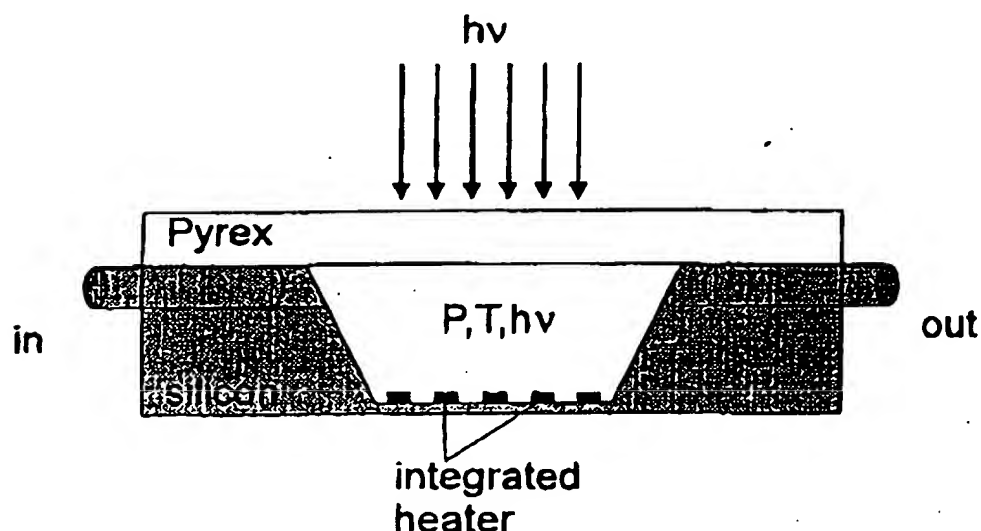


Fig. 9 Microfabricated reactor with controlled pressure, temperature and illumination.

A. van den Berg

Typical dimensions of the above-mentioned microreactors are in the order of a few square millimeters. This allows the arrangement of large numbers of them in coupled arrays. The small size of the microreactor offers a number of advantages: negligible amounts of chemical waste, no explosion danger, and fast control of temperature and pressure. Potential applications are found in the field of reaction kinetics and reaction parameter optimization for instance in organic synthesis e.g. in pharmaceutical industry (see fig. 10).

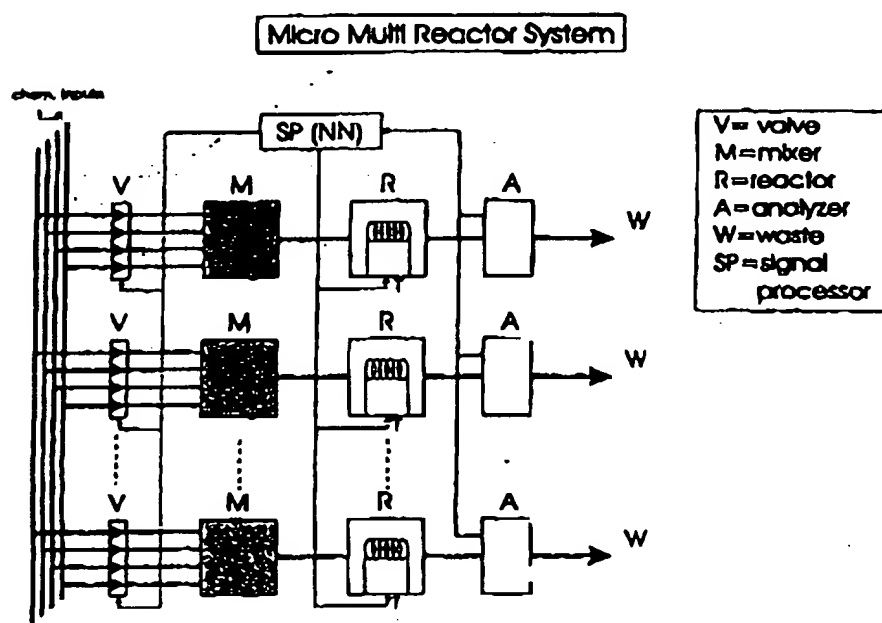


Fig. 10 Example of a microreactor array with analysis units coupled with signal processing unit for reaction parameter optimization.

In this system the valves V are controlled in such a way that the required reaction product is obtained with maximum yield. The parallel configuration of many reactors helps to increase the speed of the reaction optimization. Alternatively, products of the reactions may be fed back to the inputs of the

valve units. In this case, the dynamic behavior of coupled chemical reactions may be studied. The proposed setup can be used for both gas and liquid systems.

5. Conclusion

A modular system concept for fluid handling (Micro Fluidic System, MFS) has been proposed for the realization of micro total analysis systems and micro chemical systems. MFS enables the use of standard components or modules to be integrated on a planar base plate that contains fluid channels as well as electronic circuitry. Through the standardization the exchange of different components from different suppliers is stimulated. An example of a microreactor in the form of a microtitrator is presented and it is illustrated how incorporation of this microreactor in a micro total analysis system improves its performance and avoids some of its disadvantages. Finally an example is given of a microreactor array system for optimization of chemical reactions.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference G/84746	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NO98/00051	International filing date (day/month/year) 20/02/1998	Priority date (day/month/year) 20/02/1997
International Patent Classification (IPC) or national classification and IPC B01J3/00		
Applicant SINVENT AS et al		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 04/09/1998	Date of completion of this report 22.03.99
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Buesing, G Telephone No. (+49-89) 2399 8356 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO98/00051

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-17 as originally filed

Claims, No.:

1-17 as received on 12/01/1999 with letter of 08/01/1999

Drawings, sheets:

1/7-7/7 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO98/00051

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1, 3 - 17
	No:	Claims 2
Inventive step (IS)	Yes:	Claims
	No:	Claims 1, 3 - 17
Industrial applicability (IA)	Yes:	Claims 1 - 17
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NO98/00051

Section V:

1. Claims 1 and 2 define a multiautoclave reactor vessel in broad terms. Basically, the reactor vessel has a central block with a multitude of perforations or cavities, cover means, sealing means and locking means.

It is observed that claim 2 has to be considered as independent because it does not contain a feature which is additional to claim 1 but rather is an alternative feature (permanently closed cavities instead of through-going perforations).

2. According to the description, the invention is more specifically directed to a multiautoclave reactor which should withstand temperatures in the range between 100 and 250°C (page 4, line 34) and elevated pressures (page 3, lines 10 - 12) the range of which has not been specified in the description. Typical reactor volumes are indicated on page 6, line 36.
3. From the documents cited in the international search report, US-A-5112574 (hereinafter D1) represents the closest prior art. As seen in Fig. 9 of D1, the array of wells 18 forms a central block with a multitude of cavities permanently closed at one end and with cover means, operatively associated with sealing means, for engagement with said central block to seal the open ends of said cavities. The sealing means, which are operatively associated with the cover means, form a "pressure tight" seal when said cover means is brought into position by a locking means (reference numeral 23 in Fig. 1).

The subject-matter of claim 2 is anticipated by D1.

4. It is not apparent how the use of through-going perforations, as in claim 1, or other features of the dependent claims or the description could support an inventive step. Therefore, it is not seen which part of the application could serve as a basis for a claim defining new and inventive subject-matter.

Section VIII:

1. It is noted that the reference to "elevated pressure" in claim 1 is vague and indefinite in the absence of a definition of a suitable pressure range and is merely interpreted as any pressure above atmospheric.

PATENT CLAIMS

1. A multiautoclave reactor vessel for use at elevated pressures characterised by
 - a) a central block having a multitude of perforations, wherein said perforations are
5 through-going perforations,
 - b) cover means, operatively associated with a sealing means, for engagement with said
central block to seal the open ends of said perforations forming a multitude of
chambers,
 - c) a sealing means, operatively associated with the covers means, to form a pressure tight
10 seal when said cover means is brought into position by a locking means,
 - d) a locking means acting in concert with the cover means to engage the sealing means
so as to define a multitude of reaction chambers.
2. A multiautoclave reactor vessel as claimed in claim 1, wherein said perforations are
15 cavities or other form of holes permanently closed at one end.
3. A multiautoclave reactor vessel as claimed in claim 1, wherein said sealing means is
wholly or partly constructed of a compressible or deformable material.
- 20 4. A multiautoclave reactor vessel as claimed in claim 1, wherein said central block is
wholly or partly constructed of a compressible or deformable material.
5. A multiautoclave reactor vessel as claimed in claim 1, wherein said sealing means is
permanently fixed to the cover means.
- 25 6. A multiautoclave reactor vessel as claimed in claim 1, wherein said cover means,
acting in concert with the sealing means, has a multitude of protrusions of spherical
shape, form or profile, either in part or wholly, presenting a curved surface towards the
openings of the multitude of perforations in the central block.
- 30 7. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means
consists of spherical shaped bodies or similar shaped components, permanently fixed to
the cover means, such that they present a curved surface towards the opening of the
multitude of perforations in the central block.

35

8. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means consists of spherical shaped bodies or similar shaped components, loosely fixed to the cover means, such that they present a curved surface towards the opening of the multitude of perforations in the central block.

5 9. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be permanently fastened to the cover means.

10 10. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be loosely fastened to the cover means.

11. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means
15 consists of a flat plate or membrane, covering all the chambers, that may be permanently fastened to the cover means.

12. A multiautoclave reactor vessel as claimed in claim 1, wherein the sealing means
20 consists of a flat plate or membrane, covering all the chambers, that may be loosely fastened to the cover means.

13. A multiautoclave reactor vessel as claimed in claim 1, wherein said locking means acts in concert with a single cover means on one surface of the central block to define a multitude of cavities.

25 14. A multiautoclave reactor vessel as claimed in claim 1, wherein said locking means consists of a plurality of fasteners passing by means of appropriate holes from the upper surface of the upper cover means through the central block through to the lower surface of the lower cover means.

30 15. A multiautoclave reactor vessel as claimed in claim 1, wherein said cover means is a rigid flat plate.

35 16. A multiautoclave reactor vessel as claimed in claim 1, wherein said cover means, acting in concert with the sealing means, has a multitude of protruding profiles of dimensions sufficiently larger than the dimensions of the perforations in the central block and of cross sectional shape such that in concert with the sealing means through the action

of the locking means, a pressure tight seal is formed over and around each of the multitude of perforations in the central block.

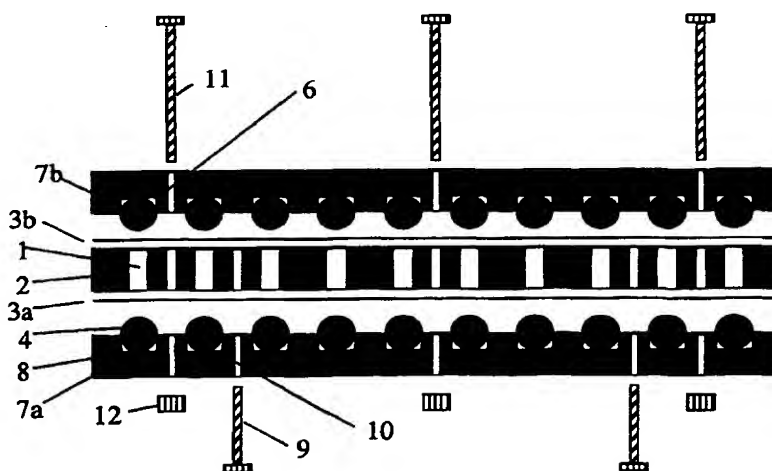
17. A multiautoclave reactor vessel as claimed in claim 1, wherein said central block,
5 acting in concert with the sealing means, has a multitude of protruding
profiles of dimensions sufficiently larger than the dimensions of the perforations and of
cross sectional shape such that in concert with the sealing means and through the action of
the locking means on the cover means, a pressure tight seal is formed over and around
each of the multitude of perforations in the central block.



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(54) Title: MULTIAUTOCLAVE FOR COMBINATORIAL SYNTHESIS OF ZEOLITES AND OTHER MATERIALS



(57) Abstract

The invention relates to a multiautoclave and details of its design and a method for automated synthesis of zeolites in said multiautoclave and, furthermore, application of the multiautoclave for an automated synthesis which is optimized simultaneously with regard to several synthesis parameters in the synthesis of zeolites. The multiautoclave consists typically of a pressure vessel/autoclave lined with an inert material with from 10 to 10.000 small, separated chambers, each typically having a volume of 0,2–2 ml, the chambers preferably being formed as through-going perforations in a central block and the perforations are sealed by means of balls, septa, stoppers or such which are placed at the bottom and top of each through-going perforation, and metal plates are placed over and under the Teflon plate so that the closing mechanism is pressed against the edges of the perforations in the Teflon plate with sufficient load to enable the chambers to be filled with aqueous mixtures and to be heated to 200 °C without the occurrence of leakage. Top- and bottom plates and closing mechanisms can be integrated so that all the perforations are sealed simultaneously when these are placed at the top and bottom sides of the central block.

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MULTIAUTOCLAVE FOR COMBINATORIAL SYNTHESIS OF ZEOLITES AND OTHER MATERIALS

FIELD OF THE INVENTION

The present invention relates to a pressure and temperature reactor vessel, especially a multiautoclave and to details concerning the design of this equipment.

BACKGROUND OF THE INVENTION

Many materials, such as e.g. zeolites, are prepared by so-called hydrothermal synthesis at temperatures ranging from 100°C to 200°C requiring crystallization times of 1 hour or more. For syntheses being carried out at temperatures that are higher than the solvent's boiling point, it is necessary to use pressure vessels, and these have to be suitable for the temperature and pressure used during the operation. The pressure vessel has to be designed so that the handling of it does not represent any unnecessary hazard, provided it is used according to working instructions.

Zeolite syntheses are usually performed in strongly alkaline media, often at pH>14, and the reaction mixture will often contain toxic chemicals, such as e.g. fluoride. Conventionally, syntheses that may be performed at temperatures lower than 110°C are carried out in polymer bottles, often Teflon, while reactions at higher temperatures require steel autoclaves, perhaps lined with Teflon. The price of an autoclave of this type with the required safety details are typically of the order of NOK 10.000,- or higher. Furthermore, such an autoclave will weigh from 1 kilogram and upwards, and all these elements represent limitations regarding the number of syntheses that may be performed in most laboratories in the course of one year.

Zeolite synthesis is often carried out by keeping the synthesis mixture at around 100°C for at least 6 h. At these moderate temperatures sealed chambers are necessary in order to avoid drying out of the synthesis mixture.

As an example of conventional zeolite synthesis, Zeolite Y can be prepared according to US 3.130.007, Example 1, by dissolving 5 g sodium aluminate containing 30 weight percent Na₂O and 44 weight percent Al₂O₃ and 22 g sodium hydroxide containing 77.5 weight percent Na₂O in 89,5 ml distilled water. This solution was added to 124.2 g of an aqueous colloidal silica sol with 29.5 weight percent SiO₂, so that the resulting mixture had a composition corresponding to 13.9 Na₂O : Al₂O₃ : 28.2 SiO₂ : 471 H₂O, and the mixture was homogenized by stirring. The mixture was enclosed in a sealed glass vessel, placed in a water bath and heated at 100°C for 21 hours, after which the product was recovered by filtering, washed and dried. Common to all the synthesis procedures

mentioned and for all other known synthesis procedures for preparation of zeolites on laboratory scale with the purpose of discovering new zeolites or to optimize existing zeolites, is that these are performed in a cumbersome and expensive manner by having to separately prepare each reaction mixture, which typically consists of 4-7 reagents, and by adding the reagents one by one.

In many other examples the synthesis of zeolites and other molsieves needs temperatures well above 100°C, so that steel pressure vessels or the like are required.

Furthermore, each reaction mixture is typically prepared in batches of 5 to 100 g and crystallized in expensive and heavy autoclaves with internal volumes often in the range of 25 to 250 ml and with weights of up to 8 kg per autoclave, causing considerable expense due to a large consumption of often expensive reagents and due to the fact that the handling of the heavy autoclaves often makes it impossible to handle more than one autoclave at the time, and finally that the size of the autoclaves limits the number of autoclaves that may be placed in each oven or heating unit. The combination of all these elements are, according to known technology, making each zeolite synthesis a very resource intensive process, and there is a great need for greater efficiency, rationalization, downscaling and automation. Simple calculations have shown that by combining the different variables which are involved in zeolite synthesis with narrow enough intervals in reagent concentrations, temperatures, reaction time, etc. to cover any phase formation based on known examples, it is feasible to make up 10^{18} recipes. With to-day's synthesis capacity, which on a global basis hardly exceeds 100.000 syntheses per annum, it would take 10.000.000.000.000 years to carry out all these syntheses in which each and every one in theory has potential for the preparation of a new zeolite or other microporous material. The expenses involved in performing these syntheses according to known technology would obviously be formidable, and there is thus a great need for new and more cost efficient methods for zeolite synthesis.

In recent years new, automated methods for systematic preparation of new compounds, so-called "combinatorial techniques", have been developed, but equipment which may be used for liquid phase synthesis at temperatures above approx. 100°C has till now not been disclosed, because this requires that the synthesis takes place in a hermetically sealed vessel at elevated pressures. WO 95/12608-A1 for instance, discloses an apparatus and a method for a) synthesis of several molecules on substrates, comprising distribution of the substrates in the reaction chambers, b) combination of the first addition of these molecules with different reagents in each of the reaction chambers, c) moving the substrates through tubing to separate mixing chambers where the substrates are mixed, d)

redistribution of the substrates by transport through tubing back to the reaction chambers, and e) combination of a second portion of different composition to the first portions of molecules in the different reaction chambers in order to prepare new mixtures. This publication describes only a system for mixing and distribution of different molecules and not a system for hermetical sealing of the reaction chambers which would make it possible to operate at high temperatures, and this system would thus not be suitable for the synthesis of zeolites. In WO 96/11878 there is a description of extensive use of a combinatorial arrangement for synthesis of new materials, including zeolite synthesis at 100°C. Even though this patent application presents a detailed description of instrumentation and equipment developed for different purposes, autoclave systems required for performing the syntheses under the prevailing physical conditions (elevated pressure and temperatures exceeding 100°C) are not described.

Prior art teaches autoclaves with several chambers for special purposes, and there is for instance in US 5.505.916 a description of a metal cassette which can be opened and closed like a suitcase, and which has an interior with compartments intended for placement of the different instruments used by dentists, where these may be sterilized by autoclaving. Furthermore, large autoclaves intended for instance for the growth of crystals, are known, examples are described in US 5.322.591, US 5.312.506 and US 5.476.635, but the purpose of these and similar autoclaves is to make it possible to carry out large-scale syntheses, for which there is a great need when a synthetic procedure has been established and scale-up is desired, or when the purpose is to grow single crystals as large as possible. The autoclave described in the earlier mentioned US 5.312.506 is designed to withstand temperatures up to 1500°C for growth of crystals from metal melts. Another feature in connection with work with autoclaves is energy savings, and this is addressed in EP 0.434.890 A1, with description of a system for insulation of the autoclave walls and for the design of such insulating layers in the walls, which could be useful for large-scale autoclaving, but is of no relevance when working with small laboratory autoclaves which are heated in ovens.

Furthermore, there is a series of known equipment intended for synthesis of proteins and biopolymers, where the design comprises sheets with a large number of chambers intended for screening of syntheses and crystal growth, in its simplest form as described in US 5.096.676. US 5.400.741 describes a diffusion cell for growth of the largest and the most perfect crystals possible of macromolecular compounds by a technique called the "hanging drop" technique. Several patents, e.g. US 5.013.531, US 5.531.185, US 5.362.325 and EPA 0.553.539 A1, deal with cells for growth of proteins and biopolymer crystals in spacecrafts. Common for the latter patents is that the designs described are

very sophisticated and thus very expensive, because they are intended for use in spacecrafts. Common for all equipment designed for synthesis and crystal growth of proteins and biopolymers is that they are meant for use at low temperatures, or typically temperatures in the range of 0°C to 65°C, and that they consequently are not designed to withstand conditions typical for hydrothermal synthesis. In addition, many of these prior art synthesis cells are not lined with Teflon or other similarly inert materials, something that almost without exceptions is required for synthesis of zeolites and the like. There is, e.g., a known design called "multiblock" (Krechnak, V., Vagner, J.; Peptide Res. 3, 182 (1990)) consisting of i) a Teflon block holding 42 reactors, polypropylene syringes equipped with polymer filters, ii) a vacuum adapter connecting each reactor to a vacuum line (not described in detail) which enables rapid washing in an apparatus for continuous flow, iii) two Teflon plates with 42 stoppers to which the Teflon block is fastened during use, and iv) a glass cover used during homogenization. The problem with this design is that the reactors which are made of glass and which do not have protected sidewalls may be used only at low pressures and not in strongly alkaline solutions. There is thus no available literature describing equipment that might be used for practical work with combinatorial zeolite synthesis, in as much as such syntheses almost without exception require hydrothermal treatment of a solution or gel with relatively high content of water and often high contents of organic compounds in a closed chamber, and almost all methods for preparation of zeolites known so far require such conditions during synthesis, and this is true without exception for all methods which have proved to be commercially applicable. The synthesis of zeolites is thus normally performed under hydrothermal conditions which require elevated pressures and high temperatures in periods up to several weeks without leakage. The problem has so far been the costs involved in this type of work, estimated to an average of NOK 5.000,- per synthesis, including recovery of the product and XRD analysis. An important feature when dealing with large series of syntheses is therefore how the product can be recovered and washed in a rational way without insurmountable expense, something that is not disclosed in prior art. As far as known, this type of work is performed in the same manner by all synthesis laboratories engaged in synthesis of zeolites and non-carbon-based molecular sieves.

One objective of the present invention has been to develop a complete system for screening of synthesis conditions for preparation of zeolites and other non-carbon materials requiring hydrothermal conditions in the temperature range 100°C to 250°C in a more cost efficient manner, and it has thus been of interest to improve a series of parameters, which means making them more cost efficient. Some of these parameters are:

1. Reduced size of the separate reaction chambers and increased number of reaction chambers what is called a multiautoclave.

This will lead to reduced use of reactants and thus cheaper synthesis.

2. Automated addition of reactants, for instance by having 100 reaction chambers present in one multiautoclave and by enabling this to be connected to a pipetting machine which makes quick and exact addition of all liquid reactants possible.

3. Simple and easy-to-use mechanism for the closing and opening of the multiautoclave.

4. Simple recovery and washing of the synthesis product and simple cleaning of the multiautoclave after use.

5. Devices allowing automated analysis with X-ray diffraction and automatic identification of known crystalline phases by combination of an automatic sample switcher, a structure library stored in a database and software that can monitor sample switching and identification.

Another objective of the present invention described here has been to design automated equipment for larger synthesis series and prepare formulations based on mixtures of different liquids/solutions with varying reactant ratios.

These and other objectives are attained by the present invention, which represents a breakthrough in terms of cost reduction for e.g. zeolite synthesis in that the reaction mixture crystallizes in a volume reduced typically to 1/100 of what has been used conventional, thereby achieving reduced consumption of reactants and cheaper syntheses, and further by enabling automated addition of reactants, e.g. by having 100 or more available reaction chambers in one single multiautoclave, and that the multiautoclave plates can be connected to a pipetting machine that makes quick and exact addition of all liquid reactants possible, and by being able to place several such plates with reaction chambers on top of each other without difficulty. Furthermore, an important feature of the present invention is the simple and not very time-consuming operation of the multiautoclave.

The present invention relates to a pressure and temperature reactor vessel comprising

- a) a central block having a multitude of perforations, wherein said perforations are through-going perforations, or cavities or other form of holes permanently closed at one end,
- b) cover means, operatively associated with a sealing means, for engagement with said central block to seal the open ends of said perforations forming a multitude of chambers,
- c) a sealing means, operatively associated with the covers means, to form a pressure tight seal when said cover means is brought into position by a locking means,
- d) a locking means acting in concert with the cover means to engage the sealing means so as to define a multitude of reaction chambers.

Applications for the present invention may, in addition to zeolite synthesis, be in any field of activities within research and development connected to products where at least one production-step comprises the mixing of different liquids, e.g. in the fields of organic and inorganic syntheses, paint production, formulation of fuels, food industry, etc., and furthermore, applications within clinical testing, dissolution and digestion of samples with acid etc. where a liquid reactant is added to a liquid or solid. The invention is in particular aimed at applications where open vessels cannot be used, and more specifically for applications where it is required to operate at temperatures which will cause elevated pressures in the liquid part of the mixture.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Further advantages and characteristic features of the present invention are illustrated in the following description by referring to the drawings which, as mere examples without limitations, show some designs related to this invention, where Figure 1 present a side-view of the multiautoclave with the single components disassembled, and Figure 2 shows a top-view of the multiautoclave, while Figure 3 shows an alternative design of the multiautoclave (side-view). Figure 4 shows a section of one of the chambers of the multiautoclave (side view) equipped with a Teflon liner and disc-shaped lids. Figure 5a shows a section of the multiautoclave in "exploded" view, and in Figure 5b in closed mode.

Figure 6 presents an example of different chemical compositions covered in one single experiment using the multiautoclave.

More specifically, the invention comprises a unit containing a multitude of pressure vessels, also referred to as a multiautoclave. This multiautoclave has typically from 10 to 10.000 or more small, separate chambers (1), each typically with a volume of 0.001 – 10 ml. The multiautoclave is composed of a set of plates (2 and 7) and optionally thin laminae (3) which are stacked so that they form a matrix of small chambers (1), as shown

in Figures 1 - 5. The thickness of the different plates and laminae may vary, always keeping in mind that a maximum number of small chambers with optimal size is desired, and that the chambers must be leak tight and dimensioned such that no excessive degree of deformation will take place under the operational conditions which the equipment is designed for. The central block consisting in a perforated plate (2), with a multitude of perforations, serve – when sandwiched between the plates (7a and 7b) and closed – as the frame of the pressure chambers, and may for use at higher temperatures (150 - 250°C) be made from stainless steel, aluminium, titanium or other rigid material s.a. PEEK or the like, with perforations of e.g. 10 mm diameters, where each perforation is lined with a segment of Teflon tubing or tubing made from another suitable polymer material, and where the walls of the linings e.g. can have a thickness of 1-3 mm. For use at temperatures below 150°C, the central block can be made entirely of Teflon, and for use below 130°C it can be made of polypropylene, and for use below 105°C it can be made of polyethylene. In the separate pressure chambers, balls (4) made from Teflon or other suitable material s.a. steel, PEEK, Nylon or glass may be used as a bottom- and toplid, also referred to as sealing means or septa (5) made from an elastomer or from another appropriate material s.a. Teflon in the shape of circular disks which will give the advantage in the form of reduced weight and volume. Septa should be made from an elastomer, preferably Viton, or other suitable material that can withstand temperatures of at least 200°C, and they may be equipped with Teflon lining (13) on the side facing the chamber as shown in Figures 4 and 5. Furthermore, said septa (5) should have a thickness considerably larger than the depth of immersion, as shown on Figure 3, in order to ensure a tight fit when assembling the different elements. As an alternative, septa or balls may be fastened on the bottom and top plates or on separate polymer films or a thin metal plate in such a way that they may be put in place and removed in a simple manner. The bottom and top plates (7) thus hold balls, septa, stoppers or other types of suitable cover means in place as the central block (2) is squeezed between the bottom and top plates. In order to avoid the use of balls, septa, stoppers or loose parts, the bottom and top plates can also be designed with a structure that has conical or hemispheric protrusions that fit into the perforations. Another design comprises polymer films moulded or otherwise shaped to cover all the perforations. In yet another design, the central block has been machined so that sharp edges (14) protrude around each perforation or well, as shown in Figure 5. The advantage of this design is that one smooth polymer sheet can be used as a lid or sealing device for all the chambers because the sharp protrusions cut into this polymer sheet so that leakage between adjacent chambers does not occur when the reaction vessel is closed with its locking mechanism. Said sharp protrusions (14) could alternatively consist of rings or e.g. a rectangular grid that are either welded onto the central block (2) or fastened by any other suitable method. These said protrusions may optionally be part of the insides

of the top (7b)- and bottom plates (7a) or the central block (2). The important point here is that the load used when assembling the different elements is concentrated just at the edges of the perforations and lids, so that liquid or vapour cannot leak out during heating.

5 In one embodiment, all plates and laminae have a series of holes drilled through (6) for locking means, which can be bolts which are used to assemble the multiautoclave and ensure a sufficient counter-pressure to prevent leakage when the liquid in the chambers is heated to high temperatures, and the bolts are placed in such a manner and their number is adjusted so that a sufficiently distributed even load is obtained in order to ensure that all
10 the chambers are tight when in use. The multiautoclave may alternatively be closed by pressing the plates against each other employing a clamping or squeezing mechanism that makes through-going bolts unnecessary. The squeezing mechanism may include springs or the like, which ensure the maintenance of a suitable pressure. A frame made of a rigid material that ensures good tightness in the outer chambers may enclose the entire
15 multiautoclave, also counteracting deformation of plates made of pure Teflon or another ductile material. Bolts and frames or whatever other locking mechanisms used are tightened with a torque wrench in order to ensure correct load throughout. A possible feature of the design is that a large number of plates may be placed on top of each other forming layers of reaction chambers according to the desired capacity. As an example, 10
20 plates with pressure chambers can be placed on top of each other without requiring a total multiautoclave thickness of more than typically 25 – 40 cm. Another important feature of this invention is that the large number of chambers which are created by the described assembly of the various described parts subsequent to performing e. g. a number of syntheses can be opened in both ends. This makes simple and efficient recovery and
25 washing of the synthesis products possible, and as an example on how this can be performed, the top plate with associated lid (e.g. septum) is removed first, and a filter paper placed over it and pressed against the plate with a sponge or another suitable absorbent or a filter supported by a rigid grid connected to a pump. The multiautoclave is then turned upside-down, and the bottom plate with associated lid is removed. The liquid
30 in the reaction chambers can then drain through the filter, and the synthesis product can be washed by flushing down through the perforations. As a result, the final, washed synthesis products are each in its own position on the filter paper, and these positions correspond to the positions of the perforations of the mainblock in the multiautoclave, so that identification of the synthesis products can be achieved. The samples are placed in a well-
35 defined matrix that, in principle, in a simple manner can be transferred to an automatic sample-switching unit for analysis, e.g. by X-ray diffraction. It is often desirable to calcine inorganic samples after synthesis, and for this purpose the samples can be washed

from the multiautoclave and into the perforations of another block which is made of a material suitable for performing calcination s.a. stainless steel or quartz.

Whenever the perforations, which on closing form the pressure chambers are going through the central block, the bottom has to be closed before charging with liquid or other reactants. This can be achieved in a simple manner by placing the perforated plate (2) on top of a plate (7a) with balls, septa or other sealing devices between them. The two plates (2 and 7a) are then bolted together with a set of bolts (9) with lengths somewhat less than the combined thickness of the two plates, so that no part of the bolts is protruding from the plate assembly. In the example shown in Figure 2, six bolts placed as illustrated have been found to be sufficient to hold the bottom plate sufficiently tight to the central block. After the chambers have been charged, the top plate (7b) with its sealing devices is put in place, and another set of bolts (11), which are considerably longer than the thickness of the entire multiautoclave, is put through a separate set of through-going holes (6) and tightened with nuts (12) at the bottom side with a torque wrench and with a load sufficient to keep the multiautoclave tight under the prevailing synthesis conditions it is going to be exposed to. Springs adjusted to a suitable pressure can, for instance, be put on the bolts before placing the nuts on them.

The advantages of the present invention are primarily related to the large rationalization gain that gives a correspondingly large economic saving. The saving is estimated to be from 90 to 99%. In other words, either the cost related to a given synthesis program is reduced by 90 - 99%, or it is possible for a given amount of money to perform 10 - 100 times as many syntheses. Such an automated layout will make it possible to perform e.g. 1000 syntheses/formulations simultaneously, and it will thus be very useful for all research laboratories, in industry as well as in research institutions/ universities.

Multiautoclaves suited for the purposes mentioned above might be designed as described in the following examples, but the descriptions are to be considered merely as examples of possible designs and the given measurements and other details shall not be considered to be limitations to the invention.

Example 1

A multiautoclave is built from 5 layers as shown in Figure 1. The different layers are placed on top of each other and bolted together so that 100 hermetically sealed chambers (1) are formed. By stacking several layers in a suitable way, it is possible to make a multiautoclave with, e.g. 1000 chambers or more. A decisive element in the invention described here is the combination of steel balls (4) and a thin polymer film (3) for the

closing of the small chambers in the multiautoclave. In as much as the contact between the edge of the perforation and the steel ball is exposed to the total pressure developed by tightening the bolts, the multiautoclave will be tight aided by slight deformation of the ductile parts.

5 The multiautoclave is from bottom to top built up from the following elements as shown in Figure 1. Bottom plate (7a) made from aluminium or steel, with 100 symmetrically positioned cavities (8), each with a diameter of 13 mm. Each cavity has a depth of 8 mm, and stainless steel balls (4) with diameters of 13 mm are placed in each cavity. In addition, the plate has 9 smaller, through-going holes (6) for bolts that are used to keep all the plates bolted together. Furthermore, a thin polymer film (3a) made of Teflon, and the purpose of this film is to tighten against the perforations in the perforated plate (2) and to avoid direct contact between the steel balls (4) and the synthesis mixtures. The polymer film has 9 smaller holes (6) through it for bolts used to keep all the plates together. 10 Further, a 2 cm thick Teflon plate (2) with 100 symmetrically positioned perforations with diameter 8 mm. In addition, the plate has 9 smaller holes (6) going through it for bolts used to keep all the plates together. There is also another set of holes (10) through the bottom plate (7a) and the perforated plate (2) that is used to keep these two plates with the corresponding balls tightly together while adding liquid. Furthermore, another thin 15 polymer film (3b) made from 0.5 mm Teflon, and the purpose and design of this film is the same as for (3a). A top plate (7b) is placed above this, identical to the bottom plate (7a), but inverted in relation to it.

20 A frame ensuring good tightening of the outer chambers by preventing lateral deformation of the Teflon block (2) is fastened around the multiautoclave (not shown).

Example 2

In another embodiment, a multiautoclave was designed and built as shown in Figure 3. In this case, Teflon-lined septa (5) type "MICROSEP F138" from Alltech which are stable 30 up to 250°C were used as bottom- and top-lids for each of the small chambers.

The multiautoclave was constructed from the following elements according to Figure 3. A bottom aluminium plate (7a), 2 cm thick with 9 smaller, through-going holes for bolts (11) used for holding all the plates bolted together. Above this plate a 2 cm thick Teflon plate with 100 symmetrically positioned perforations with diameters 8 mm is mounted. 35

Further, above and below each perforation there is a 1 mm deep recess with diameter 13 mm where Teflon-lined septa (5) with thickness of 2 mm are placed. This plate also has 9 smaller, through-going holes for bolts used to keep all the plates bolted together. There is

also a set of 6 holes (10) with associated bolts (9) used to hold the bottom plate (7a) and the central block (2) together.

An upper aluminium plate (7b), 2 cm thick, is placed on top. This plate also has 9 smaller, through-going holes for bolts (11) used to keep all the plates bolted together.

In order to test the designed multiautoclave, the bottom plate (7a) and the central block (2) (Figure 3) were bolted together so that a plate with 100 wells and solid bottom embedding the septa (5) was formed. The resulting were each filled with 0.5 ml water, and a top plate with the associated septa was fastened to it by bolts. The multiautoclave was then placed in a heating cabinet at 150°C for three days. When the multiautoclave was opened after three days, the liquid levels in the 100 chambers were unchanged.

Example 3

In yet another embodiment, a heavy duty multiautoclave was designed and built essentially as shown in Figure 3, but in this case the 20 mm thick central block (2) was made of 316-stainless steel with 13.75 mm wells which were 19 mm deep. The remaining 1 mm of the plate was drilled through with a diameter of 12.45 mm resulting in a design, essentially, as displayed in Figure 4. The 13.75 mm perforations were lined with Teflon cylinders (13) with 2.75 mm wall thickness and 18 mm length so that above and below each cylinder there is a 1 mm deep recess with diameter 13.75 in one end and 12.45 in the other end. 3 mm thick Teflon disks with 13.75 mm and 12.45 mm diameters, respectively, (5) were used as bottom- and top lids for each of the small chambers.

Example 4

The bottom plate (7a) and the central block (2) of the multiautoclave described in Example 2 with septa (5) embedded were bolted together so that a plate with 100 wells with solid bottom was formed. This plate was then connected to an automatic pipetting machine of the "Tecan miniprepTM" type which was programmed to dispense the desired amounts from 4 different solutions to each of the 100 wells, so that a total of 100 reaction mixtures with different compositions was prepared in about 30 min.

Example 5

A multiautoclave as described in Example 1 was used for 64 zeolite syntheses based on 56 different gel compositions derived from 4 different solutions, including water, so that it covered the composition range for the Na - Si - Al system shown in Figure 6. The matrix had 64 points, but 8 of these were excluded because they appeared outside the desired range. The 8 spare chambers were instead used for reproductions, so that the total

number of different compositions were 56, and these 56 compositions are given as molecular ratios in Table 1 and as volume units in Table 2, and the last 5 columns in Table 2 are volume units adjusted so that each small synthesis chamber will contain an exact volume of 0.5 ml synthesis mixture.

The four solutions were prepared so that all Si is dissolved in solution no. 4 and all Al is dissolved in solution no. 1. Solution no.1 also contains an amount of NaOH sufficient to keep Al dissolved as well as water as solvent. Solution no. 3 was used to make-up the NaOH concentration (corrected for Na content in solutions no. 1 and no. 4), and finally, water was used to make-up the amount of water required for the recipe. All solutions were normalized to 500 μ l. The compositions of the four solutions were:

1. 100 g NaAlO_2 + 8.5 g NaOH + 391.5 g water
2. 21.8 g NaOH + 100 g water
3. Water
4. Ludox LS-30 which is 30% silica sol in water

The solutions were prepared in the order and amounts given in Table 1, and automatic pipettes were used for charging the multiautoclave chambers with the solutions. Four gel compositions were chosen as reproductions, and three parallels of these were made in the multiautoclave and, in addition, a larger scale (approx. 40 g gel) synthesis was performed in a separate plastic flask as a control of the possible effects of down- or up scaling. The four reproductions were chosen so that they represented points in the range of the four zeolitic phases FAU, CHA, GML and LTA given in Figure 4.5.c on page 70 in "Zeolite Molecular Sieves, Structure Chemistry and Use" by D. W. Breck, 1974, Wiley and Sons, New York.

The multiautoclave was placed in a heating cabinet after being kept over-night at room temperature. It was opened after 93 hours of crystallization at 100°C, and it was established that all 64 chambers had stayed tight without leakage, and a large filter paper was placed so that it covered the 64 perforations and a moisture absorbing material was pressed against the outside of the filter paper so that remaining moisture was separated from the crystalline products. The products were washed by adding a small aliquot of water (ca. 0.5 ml) to each perforation for washing. Thereafter, when the solid material was transferred to the filter paper, the perforated Teflon plate was removed and the 64 filter "cakes" were transferred to 64 separate glass sample vials. The samples were then dried at 100°C in a drying cabinet.

TABLE 1

SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	SiO ₂ /Na ₂ O	sum	SiO ₂	Na ₂ O	Al ₂ O ₃	H ₂ O
1.0	1.5	0.654	3.53	0.283	0.433	0.283	19.0
1.0	1.9	0.526	3.90	0.256	0.487	0.256	19.0
1.0	2.4	0.417	4.40	0.227	0.545	0.227	19.0
1.0	3.0	0.333	5.00	0.200	0.600	0.200	19.0
1.0	4.0	0.250	6.00	0.167	0.667	0.167	19.0
1.5	1.5	0.980	4.03	0.372	0.380	0.248	19.0
1.5	1.9	0.789	4.40	0.341	0.432	0.227	19.0
1.5	2.4	0.625	4.90	0.306	0.490	0.204	19.0
1.5	3.0	0.500	5.50	0.273	0.545	0.182	19.0
1.5	4.0	0.375	6.50	0.231	0.615	0.154	19.0
1.5	5.3	0.283	7.80	0.192	0.679	0.128	19.0
1.5	8.0	0.188	10.50	0.143	0.762	0.095	19.0
2.3	1.5	1.503	4.83	0.476	0.317	0.207	19.0
2.3	1.9	1.211	5.20	0.442	0.365	0.192	19.0
2.3	2.4	0.958	5.70	0.404	0.421	0.175	19.0
2.3	3.0	0.767	6.30	0.365	0.476	0.159	19.0
2.3	4.0	0.575	7.30	0.315	0.548	0.137	19.0
2.3	5.3	0.434	8.60	0.267	0.616	0.116	19.0
2.3	8.0	0.288	11.30	0.204	0.708	0.088	19.0
2.8	1.5	1.830	5.33	0.525	0.287	0.188	19.0
2.8	1.9	1.474	5.70	0.491	0.333	0.175	19.0
2.8	2.4	1.167	6.20	0.452	0.387	0.161	19.0
2.8	3.0	0.933	6.80	0.412	0.441	0.147	19.0
2.8	4.0	0.700	7.80	0.359	0.513	0.128	19.0
2.8	5.3	0.528	9.10	0.308	0.582	0.110	19.0
2.8	8.0	0.350	11.80	0.237	0.678	0.085	19.0
4.0	1.5	2.614	6.53	0.613	0.234	0.153	19.0
4.0	1.9	2.105	6.90	0.580	0.275	0.145	19.0
4.0	2.4	1.667	7.40	0.541	0.324	0.135	19.0
4.0	3.0	1.333	8.00	0.500	0.375	0.125	19.0
4.0	4.0	1.000	9.00	0.444	0.444	0.111	19.0
4.0	5.3	0.755	10.30	0.388	0.515	0.097	19.0
4.0	8.0	0.500	13.00	0.308	0.615	0.077	19.0
4.0	12.0	0.333	17.00	0.235	0.706	0.059	19.0
6.0	1.5	3.922	8.53	0.703	0.179	0.117	19.0
6.0	1.9	3.158	8.90	0.674	0.213	0.112	19.0
6.0	2.4	2.500	9.40	0.638	0.255	0.106	19.0
6.0	3.0	2.000	10.00	0.600	0.300	0.100	19.0
6.0	4.0	1.500	11.00	0.545	0.364	0.091	19.0
6.0	5.3	1.132	12.30	0.488	0.431	0.081	19.0
6.0	8.0	0.750	15.00	0.400	0.533	0.067	19.0
6.0	12.0	0.500	19.00	0.316	0.632	0.053	19.0
10.0	1.5	6.536	12.53	0.798	0.122	0.080	19.0
10.0	1.9	5.263	12.90	0.775	0.147	0.078	19.0
10.0	2.4	4.167	13.40	0.746	0.179	0.075	19.0
10.0	3.0	3.333	14.00	0.714	0.214	0.071	19.0
10.0	4.0	2.500	15.00	0.667	0.267	0.067	19.0
10.0	5.3	1.887	16.30	0.613	0.325	0.061	19.0
10.0	8.0	1.250	19.00	0.526	0.421	0.053	19.0
10.0	12.0	0.833	23.00	0.435	0.522	0.043	19.0
20.0	1.5	13.072	22.53	0.888	0.068	0.044	19.0
20.0	2.4	8.333	23.40	0.855	0.103	0.043	19.0
20.0	4.0	5.000	25.00	0.800	0.160	0.040	19.0
20.0	5.3	3.774	26.30	0.760	0.202	0.038	19.0
20.0	8.0	2.500	29.00	0.690	0.276	0.034	19.0
20.0	12.0	1.667	33.00	0.606	0.364	0.030	19.0

TABLE 2

volume units of solution

microliter solution

ludox LS-30	soln 1	soln 2	vann	sum	factor	ludox LS-30	soln 1	soln 2	vann	sum	
46.82415	221.8	8.8032	80.2	357.68	1.398	65.45573	310.122	12.306	112.117	500	
42.38186	200.8	44.782	67.85	355.81	1.405	59.55614	282.17	62.928	95.3453	500	
37.56574	178	83.788	54.46	353.79	1.413	53.08987	251.534	118.41	76.963	500	
33.05785	156.6	120.3	41.92	351.9	1.421	46.97017	222.539	170.92	59.566	500	
27.54821	130.5	164.92	26.6	349.59	1.43	39.40061	186.676	235.88	38.0473	500	
61.52206	194.3	7.5557	95.47	358.87	1.393	85.71586	270.741	10.527	133.016	500	
56.34861	178	39.551	83.24	357.12	1.4	78.89315	249.191	55.374	116.541	500	R
50.59875	159.8	75.11	69.64	355.17	1.408	71.23129	224.99	105.74	98.0404	500	
45.07889	142.4	109.25	56.59	353.3	1.415	63.79643	201.507	154.61	80.0876	500	
38.14367	120.5	152.14	40.19	350.95	1.425	54.34291	171.647	216.75	57.2603	500	
31.7864	100.4	191.45	25.16	348.8	1.433	45.56532	143.922	274.45	36.0653	500	
23.61275	74.58	242	5.832	346.03	1.445	34.11934	107.769	349.68	8.42692	500	
78.70917	162.1	6.0969	113.3	360.27	1.388	109.2369	225.022	8.4616	157.279	500	
73.10871	150.6	33.273	101.7	358.69	1.394	101.9118	209.933	46.382	141.773	500	
66.69566	137.4	64.393	88.4	356.87	1.401	93.4441	192.49	90.218	123.848	500	
60.3437	124.3	95.216	75.22	355.08	1.408	84.9719	175.038	134.08	105.913	500	
52.07744	107.3	135.33	58.06	352.75	1.417	73.81736	152.06	191.82	82.3009	500	
44.20527	91.06	173.53	41.73	350.52	1.426	63.05645	129.893	247.53	59.5215	500	
33.64295	69.3	224.78	19.81	347.54	1.439	48.40187	99.7054	323.39	28.4998	500	
86.83113	146.9	5.4075	121.8	360.93	1.385	120.2887	203.541	7.4911	168.68	500	
81.19472	137.4	30.245	110.6	359.44	1.391	112.9455	191.115	42.072	153.867	500	
74.64676	126.3	59.099	97.66	357.72	1.398	104.3381	176.551	82.606	136.505	500	
68.06028	115.2	88.123	84.63	355.98	1.405	95.59593	161.758	123.78	118.871	500	
59.3346	100.4	126.57	67.37	353.68	1.414	83.88217	141.937	178.94	95.2423	500	
50.85823	86.06	163.93	50.6	351.44	1.423	72.35622	122.434	233.22	71.9928	500	
39.22118	66.37	215.2	27.58	348.38	1.435	56.29159	95.2511	308.87	39.5881	500	
101.2492	119.9	4.1838	136.7	362.1	1.381	139.8085	165.599	5.7771	188.815	500	
95.81986	113.5	24.767	126.7	360.81	1.386	132.7847	157.28	34.322	175.614	500	R
89.34554	105.8	49.312	114.8	359.27	1.392	124.3431	147.281	68.629	159.748	500	
82.64463	97.89	74.717	102.4	357.68	1.398	115.5296	136.841	104.45	143.182	500	
73.46189	87.01	109.53	85.49	355.49	1.406	103.3234	122.384	154.05	120.24	500	
64.19	76.03	144.68	68.39	353.29	1.415	90.84579	107.604	204.76	96.788	500	
50.85823	60.24	195.22	43.8	350.12	1.428	72.62926	86.0273	278.79	62.5493	500	
38.89159	46.07	240.59	21.73	347.28	1.44	55.99491	66.3244	346.4	31.2843	500	
116.2644	91.81	2.9093	152.3	363.32	1.376	160.0031	126.346	4.0038	209.647	500	
111.431	87.99	18.92	143.9	362.27	1.38	153.7963	121.445	26.114	198.645	500	
105.5038	83.31	38.554	133.6	360.98	1.385	146.1356	115.396	53.402	185.067	500	
99.17355	78.31	59.523	122.6	359.6	1.39	137.8934	108.887	82.762	170.457	500	R
90.15778	71.19	89.388	106.9	357.64	1.398	126.0449	99.531	124.97	149.456	500	
80.62891	63.67	120.95	90.32	355.57	1.406	113.38	89.5303	170.08	127.007	500	
66.1157	52.21	169.03	65.06	352.41	1.419	93.80433	74.0723	239.81	92.309	500	
52.19661	41.22	215.13	40.84	349.39	1.431	74.69769	58.9848	307.88	58.4422	500	
131.9148	62.5	1.581	168.6	364.59	1.371	180.9081	85.7122	2.1682	231.212	500	
128.1312	60.71	12.665	162.3	363.83	1.374	176.0871	83.428	17.406	223.079	500	
123.3502	58.44	26.672	154.4	362.87	1.378	169.9663	80.5281	36.751	212.754	500	
118.0638	55.94	42.159	145.6	361.8	1.382	163.1606	77.3036	58.262	201.274	500	
110.1928	52.21	65.217	132.6	360.22	1.388	152.9531	72.4674	90.525	184.055	500	
101.4045	48.04	90.964	118	358.45	1.395	141.4491	67.017	126.89	164.649	500	
86.99435	41.22	133.18	94.16	355.55	1.406	122.3386	57.9626	187.29	132.411	500	
71.86489	34.05	177.5	69.09	352.5	1.418	101.9356	48.2959	251.77	97.9937	500	
146.7281	34.76	0.3237	184	365.79	1.367	200.5611	47.5118	0.4424	251.485	500	
141.2729	33.47	14.739	175.3	364.76	1.371	193.6507	45.8747	20.203	240.271	500	
132.2314	31.32	38.63	160.9	363.05	1.377	182.1111	43.1411	53.201	221.546	500	
125.6953	29.78	55.901	150.4	361.81	1.382	173.7011	41.1488	77.25	207.9	500	
113.9926	27	86.824	131.8	359.6	1.39	158.4988	37.5475	120.72	183.231	500	R
100.1753	23.73	123.33	109.7	356.99	1.401	140.3068	33.2379	172.74	153.712	500	

R = point reproduced

Example 6

In another embodiment, pre-mixed gels of aluminumphosphate, silicoaluminumphosphate and cobaltaluminumphosphate were prepared and administered by means of the "Tecan MiniprepTM" to the 100 cavities of the multiautoclave of example 3. Thereafter 6 different organic compounds were added according to the molar ratios specified in Table 3. The multiautoclave was then closed and was heated for 48 h in an oven at 200°C. The solid synthesis products were recovered as described in example 5 and were dried overnight at ambient temperatures. The products were characterised by X-ray diffraction using a Siemens D-5000 diffractometer equipped with PSD detector and an automatic sample shifter. Several different crystalline phases were identified among the products including those of the structures AFI, ERI and CHA.

TABLE 3

Position	Mols AlPO gel	Mols SAPO gel	Mols CoAPO gel	R1	Mols R1	R2	Mols R2
1	1	0	0	CYCLOHEXY	1	-	0
2	1	0	0	MORPHOLIN	1	-	0
3	1	0	0	TRIPROPYL	1	-	0
4	1	0	0	DI-N-PROP	1	-	0
5	1	0	0	TEAOH	1	-	0
6	1	0	0	TRIETHYLA	1	-	0
7	0	1	0	CYCLOHEXY	1	-	0
8	0.25	0.75	0	CYCLOHEXY	1	-	0
9	0.5	0.5	0	CYCLOHEXY	1	-	0
10	0	1	0	MORPHOLIN	1	-	0
11	0.25	0.75	0	MORPHOLIN	1	-	0
12	0.5	0.5	0	MORPHOLIN	1	-	0
13	0	1	0	TRIPROPYL	1	-	0
14	0.25	0.75	0	TRIPROPYL	1	-	0
15	0.5	0.5	0	TRIPROPYL	1	-	0
16	0	1	0	DI-N-PROP	1	-	0
17	0.25	0.75	0	DI-N-PROP	1	-	0
18	0.5	0.5	0	DI-N-PROP	1	-	0
19	0	1	0	TEAOH	1	-	0
20	0.25	0.75	0	TEAOH	1	-	0
21	0.5	0.5	0	TEAOH	1	-	0
22	0	1	0	TRIETHYLA	1	-	0
23	0.25	0.75	0	TRIETHYLA	1	-	0
24	0.5	0.5	0	TRIETHYLA	1	-	0
25	0	0	1	CYCLOHEXY	1	-	0
26	0.25	0	0.75	CYCLOHEXY	1	-	0
27	0.5	0	0.5	CYCLOHEXY	1	-	0
28	0	0	1	MORPHOLIN	1	-	0
29	0.25	0	0.75	MORPHOLIN	1	-	0
30	0.5	0	0.5	MORPHOLIN	1	-	0
31	0	0	1	TRIPROPYL	1	-	0
32	0.25	0	0.75	TRIPROPYL	1	-	0
33	0.5	0	0.5	TRIPROPYL	1	-	0
34	0	0	1	DI-N-PROP	1	-	0
35	0.25	0	0.75	DI-N-PROP	1	-	0
36	0.5	0	0.5	DI-N-PROP	1	-	0
37	0	0	1	TEAOH	1	-	0
38	0.25	0	0.75	TEAOH	1	-	0
39	0.5	0	0.5	TEAOH	1	-	0
40	0	0	1	TRIETHYLA	1	-	0
41	0.25	0	0.75	TRIETHYLA	1	-	0
42	0.5	0	0.5	TRIETHYLA	1	-	0
43	0	0.25	0.75	CYCLOHEXY	1	-	0
44	0	0.5	0.5	CYCLOHEXY	1	-	0
45	0	0.75	0.25	CYCLOHEXY	1	-	0
46	0	0.25	0.75	MORPHOLIN	1	-	0
47	0	0.5	0.5	MORPHOLIN	1	-	0
48	0	0.75	0.25	MORPHOLIN	1	-	0
49	0	0.25	0.75	TRIPROPYL	1	-	0

Table 3, gel compositions for MeAPO syntheses, continued.

Position	Mols AlPO gel	Mols SAPO gel	Mols CoAPO gel	R1	Mols R1	R2	Mols R2
50	0	0.5	0.5	TRIPROPYL	1	-	0
51	0	0.75	0.25	TRIPROPYL	1	-	0
52	0	0.25	0.75	DI-N-PROP	1	-	0
53	0	0.5	0.5	DI-N-PROP	1	-	0
54	0	0.75	0.25	DI-N-PROP	1	-	0
55	0	0.25	0.75	TEAOH	1	-	0
56	0	0.5	0.5	TEAOH	1	-	0
57	0	0.75	0.25	TEAOH	1	-	0
58	0	0.25	0.75	TRIETHYLA	1	-	0
59	0	0.5	0.5	TRIETHYLA	1	-	0
60	0	0.75	0.25	TRIETHYLA	1	-	0
61	0	0	1	CYCLOHEXY	0.25	MORPHOLIN	0.75
62	0	0	1	CYCLOHEXY	0.25	TRIPROPYL	0.75
63	0	0	1	CYCLOHEXY	0.25	DI-N-PROP	0.75
64	0	0	1	CYCLOHEXY	0.25	TEAOH	0.75
65	0	0	1	CYCLOHEXY	0.25	TRIETHYLA	0.75
66	0	0	1	MORPHOLIN	0.25	TRIPROPYL	0.75
67	0	0	1	MORPHOLIN	0.25	DI-N-PROP	0.75
68	0	0	1	MORPHOLIN	0.25	TEAOH	0.75
69	0	0	1	MORPHOLIN	0.25	TRIETHYLA	0.75
70	0	0	1	TRIPROPYL	0.25	DI-N-PROP	0.75
71	0	0	1	TRIPROPYL	0.25	TEAOH	0.75
72	0	0	1	TRIPROPYL	0.25	TRIETHYLA	0.75
73	0	0	1	DI-N-PROP	0.25	TEAOH	0.75
74	0	0	1	DI-N-PROP	0.25	TRIETHYLA	0.75
75	0	0	1	TEAOH	0.25	TRIETHYLA	0.75
76	0	0	1	CYCLOHEXY	0.75	MORPHOLIN	0.25
77	0	0	1	CYCLOHEXY	0.75	TRIPROPYL	0.25
78	0	0	1	CYCLOHEXY	0.75	DI-N-PROP	0.25
79	0	0	1	CYCLOHEXY	0.75	TEAOH	0.25
80	0	0	1	CYCLOHEXY	0.75	TRIETHYLA	0.25
81	0	0	1	MORPHOLIN	0.75	TRIPROPYL	0.25
82	0	0	1	MORPHOLIN	0.75	DI-N-PROP	0.25
83	0	0	1	MORPHOLIN	0.75	TEAOH	0.25
84	0	0	1	MORPHOLIN	0.75	TRIETHYLA	0.25
85	0	0	1	TRIPROPYL	0.75	DI-N-PROP	0.25
86	0	0	1	TRIPROPYL	0.75	TEAOH	0.25
87	0	0	1	TRIPROPYL	0.75	TRIETHYLA	0.25
88	0	0	1	DI-N-PROP	0.75	TEAOH	0.25
89	0	0	1	DI-N-PROP	0.75	TRIETHYLA	0.25
90	0	0	1	TEAOH	0.75	TRIETHYLA	0.25
91-100				Reproductions chosen at random from compositions 1 - 90			

CYCLOHEX = Cyclohexylamine

MORPHOLI = morpholine

5 TRIPROPYL = tripropylamine

DI-N-PROP = dipropylamine

TEAOH = tetraethylammonium hydroxide

TRIETHYLA = triethylamine

PATENT CLAIMS

1. A pressure and temperature reactor vessel comprising

a) a central block having a multitude of perforations, wherein said perforations are
5 through-going perforations, or cavities or other form of holes permanently closed at one end,

b) cover means, operatively associated with a sealing means, for engagement with said central block to seal the open ends of said perforations forming a multitude of chambers,

c) a sealing means, operatively associated with the covers means, to form a pressure tight seal when said cover means is brought into position by a locking means,

d) a locking means acting in concert with the cover means to engage the sealing means so as to define a multitude of reaction chambers.

2. A pressure and temperature reactor vessel as claimed in claim 1, wherein said perforations are through-going perforations.

3. A pressure and temperature reactor vessel as claimed in claim 1, wherein said sealing means is wholly or partly constructed of a compressible or deformable material.

4. A pressure and temperature reactor vessel as claimed in claim 1, wherein said central block is wholly or partly constructed of a compressible or deformable material.

5. A pressure and temperature reactor vessel as claimed in claim 1, wherein said sealing means is permanently fixed to the cover means.

6. A pressure and temperature reactor vessel as claimed in claim 1, wherein said cover means, acting in concert with the sealing means, has a multitude of protrusions of spherical shape, form or profile, either in part or wholly, presenting a curved surface towards the openings of the multitude of perforations in the central block.

7. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of spherical shaped bodies or similar shaped components, permanently fixed to the cover means, such that they present a curved surface towards the opening of the multitude of perforations in the central block.

8. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of spherical shaped bodies or similar shaped components, loosely fixed to

the cover means, such that they present a curved surface towards the opening of the multitude of perforations in the central block.

9. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be permanently fastened to the cover means.

10. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be loosely fastened to the cover means.

11. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of a flat plate or membrane, covering all the chambers, that may be permanently fastened to the cover means.

12. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of a flat plate or membrane, covering all the chambers, that may be loosely fastened to the cover means.

13. A pressure and temperature reactor vessel as claimed in claim 1, wherein said locking means acts in concert with a single cover means on one surface of the central block to define a multitude of cavities.

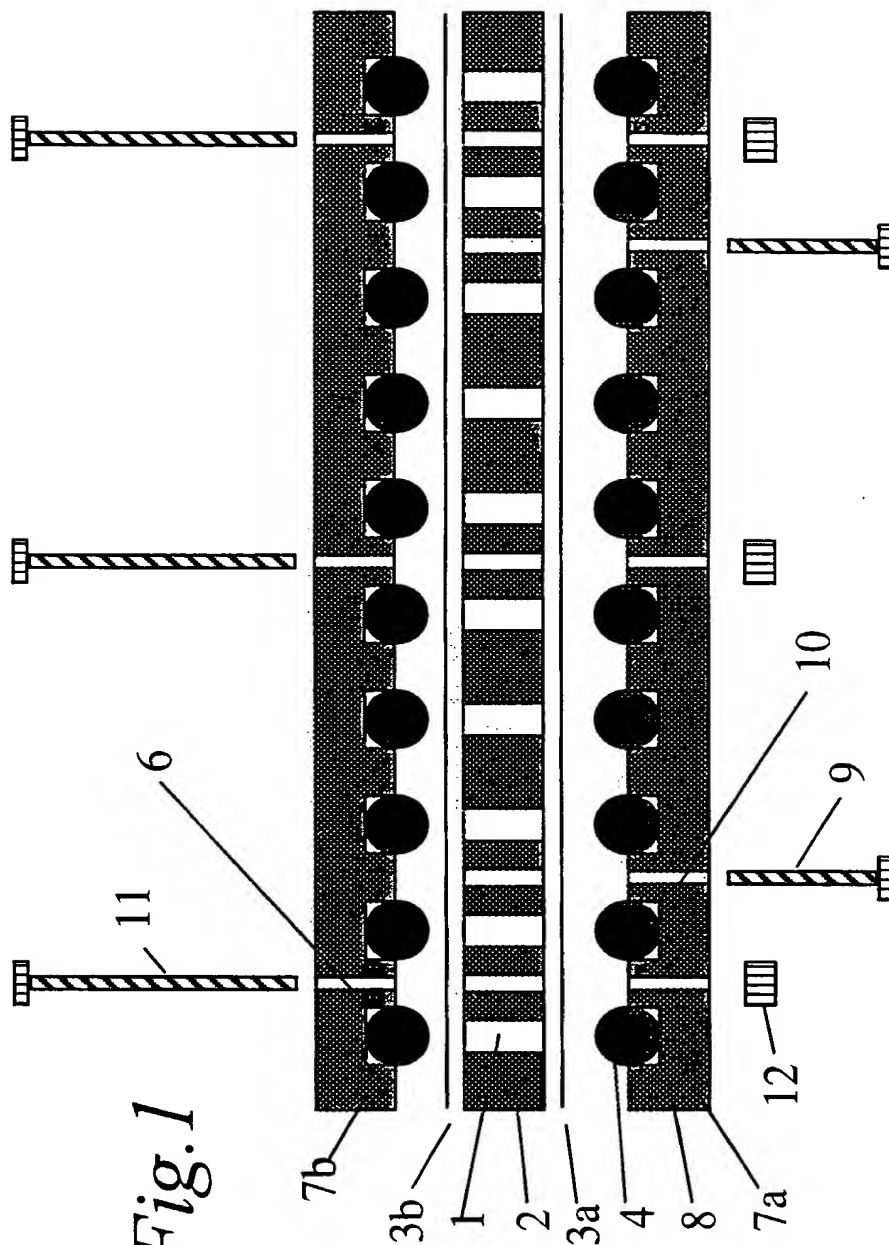
14. A pressure and temperature reactor vessel as claimed in claim 1, wherein said locking means consists of a plurality of fasteners passing by means of appropriate holes from the upper surface of the upper cover means through the central block through to the lower surface of the lower cover means.

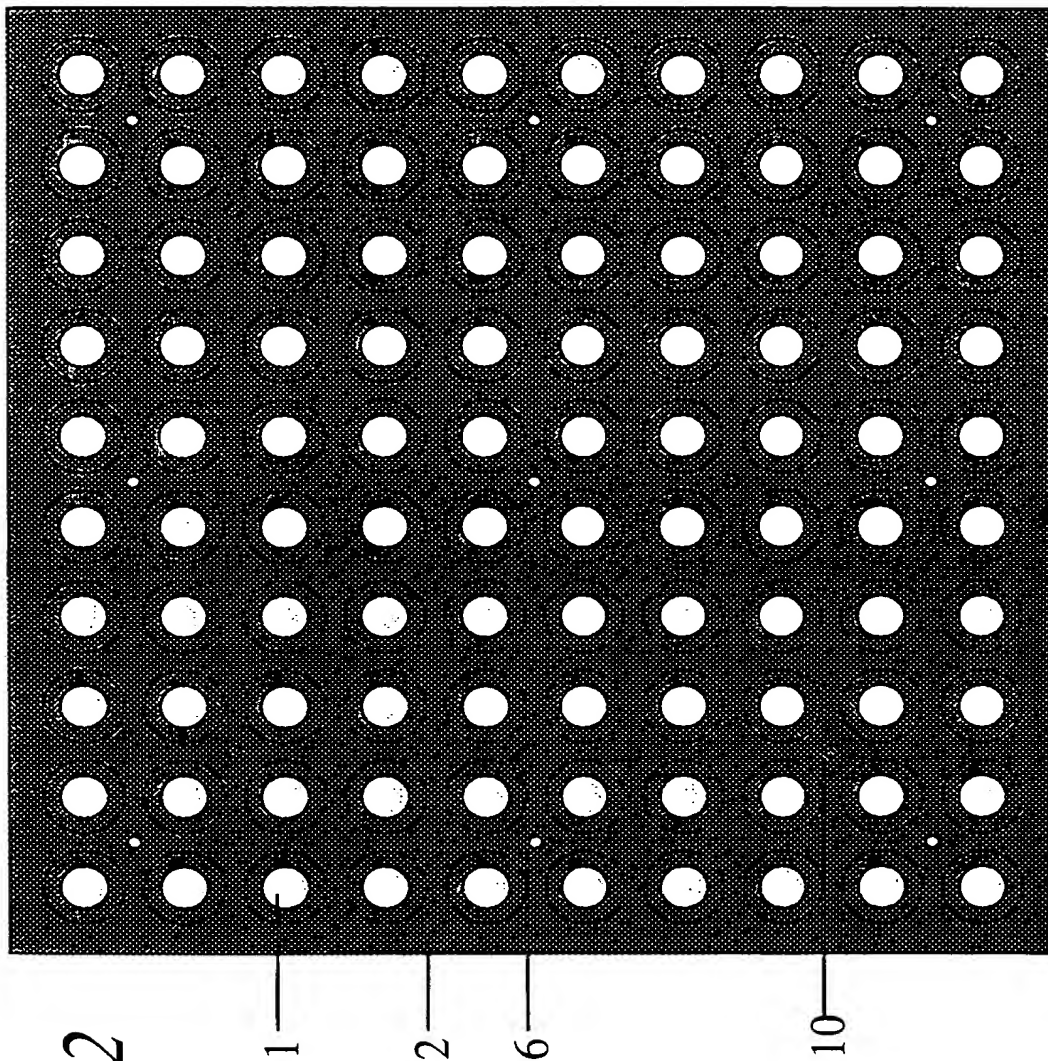
15. A pressure and temperature reactor vessel as claimed in claim 1, wherein said cover means is a rigid flat plate.

16. A pressure and temperature reactor vessel as claimed in claim 1, wherein said cover means, acting in concert with the sealing means, has a multitude of protruding profiles of dimensions sufficiently larger than the dimensions of the perforations in the central block and of cross sectional shape such that in concert with the sealing means through the action of the locking means, a pressure tight seal is formed over and around each of the multitude of perforations in the central block.

17. A pressure and temperature reactor vessel as claimed in claim 1, wherein said central block, acting in concert with the sealing means, has a multitude of protruding profiles of dimensions sufficiently larger than the dimensions of the perforations and of cross sectional shape such that in concert with the sealing means and through the action of the locking means on the cover means, a pressure tight seal is formed over and around each of the multitude of perforations in the central block.

• Fig. 1





• Fig. 2

• Fig. 3

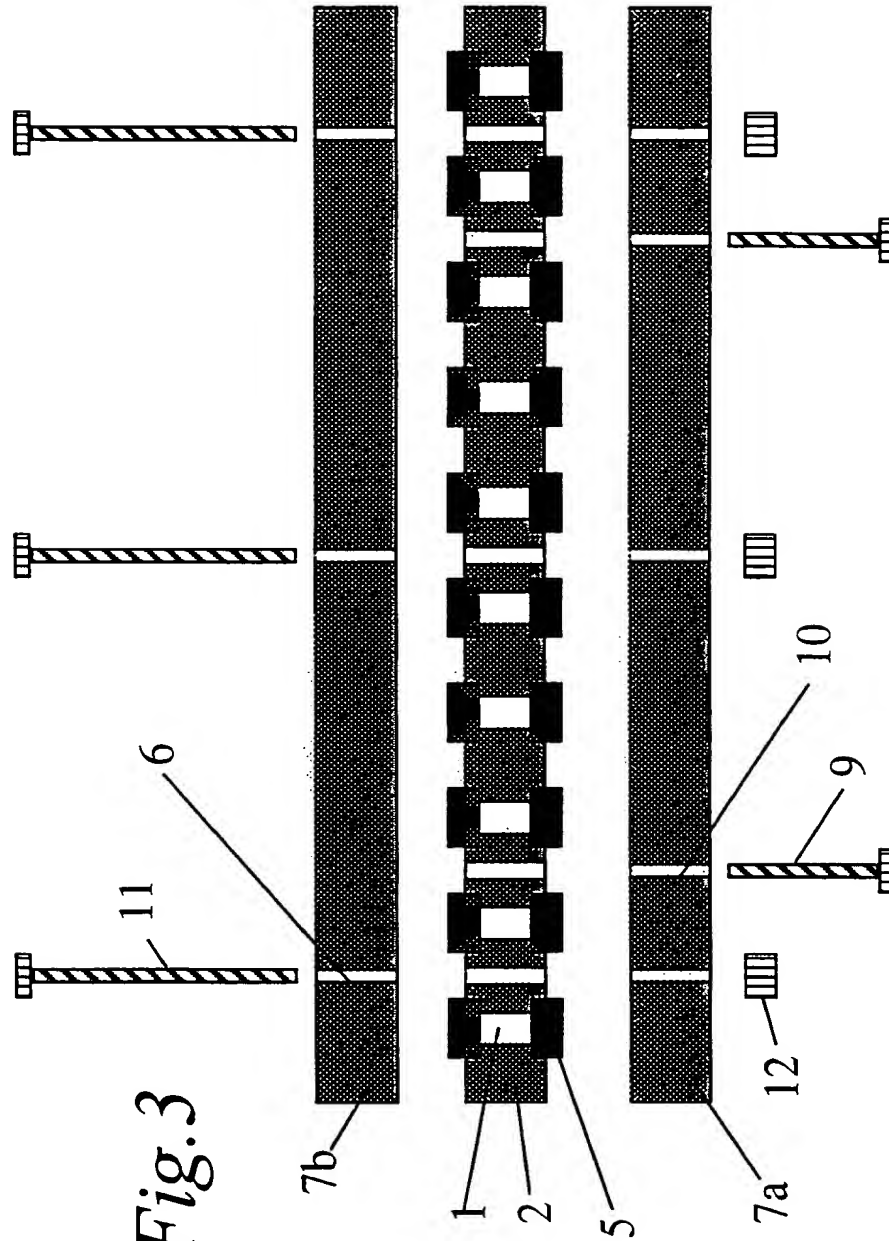


Fig. 4

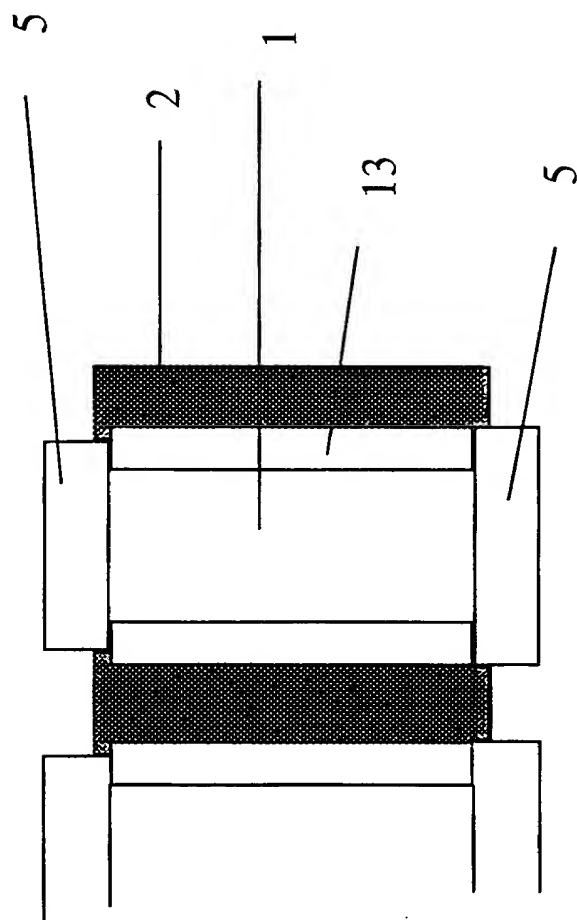
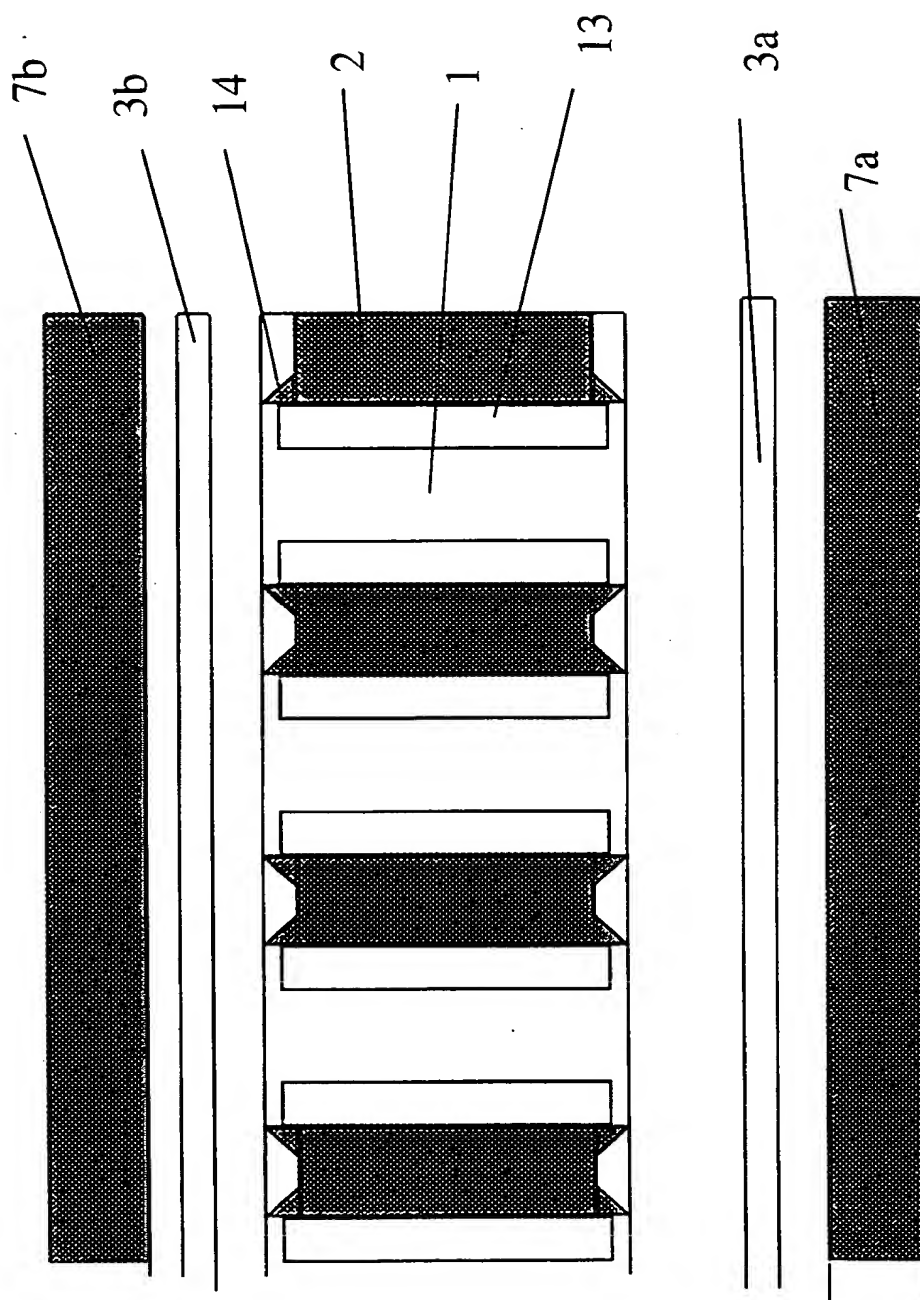


Fig 5a



6/7

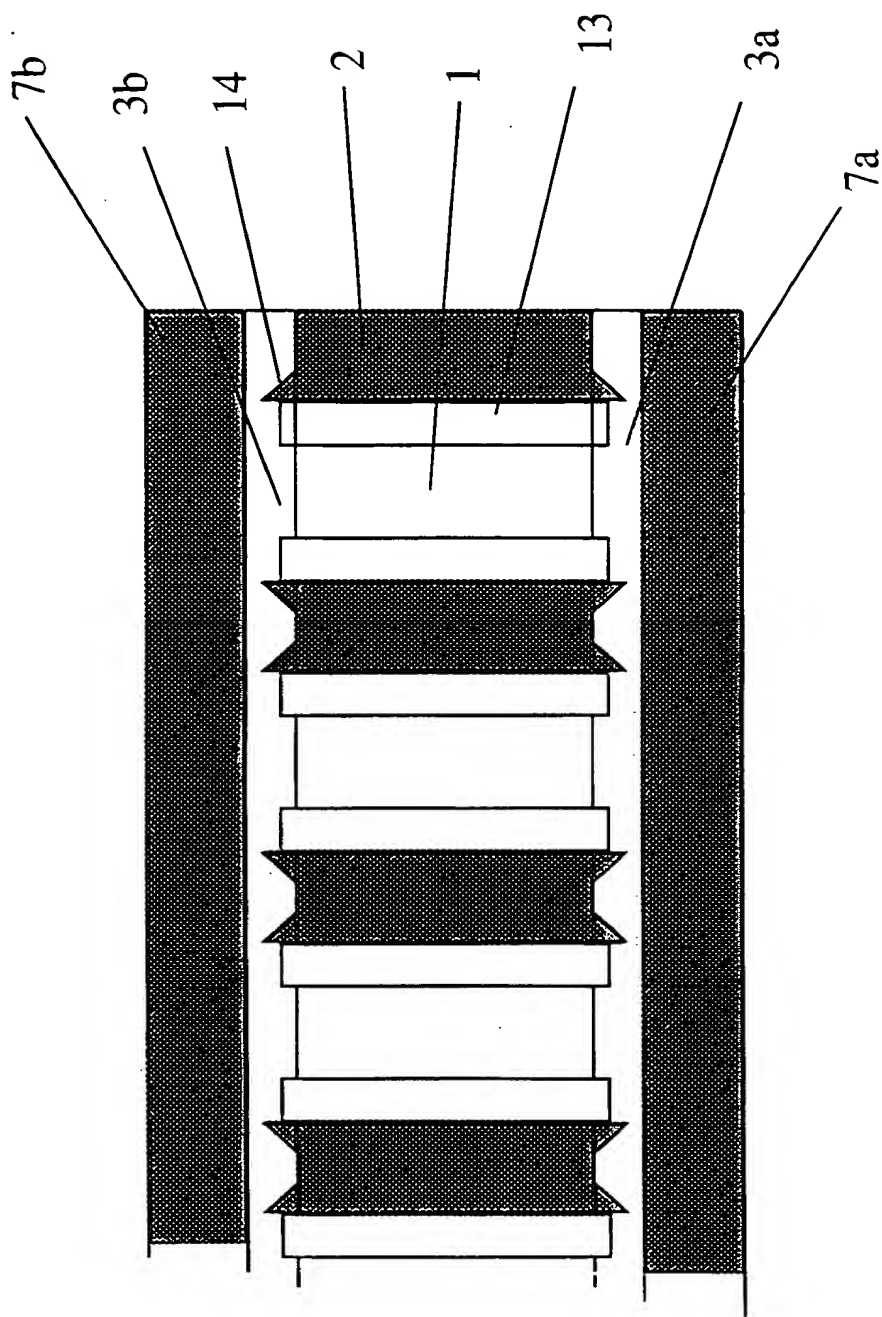


Fig. 5b

Fig. 6



O

0,5

1

$$\text{Na}_2\text{O}$$
$$\text{Al}_2\text{O}_3$$

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00051

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 3/00, C30B 29/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J, C01B, C30B, F17C, F16J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5112574 A (NIKKI HORTON), 12 May 1992 (12.05.92), column 3, line 65 - column 4, line 4, figures 1-4,9, abstract --	1-17
Y	US 5505916 A (BERNIE B. BERRY, JR.), 9 April 1996 (09.04.96), column 6, line 3 - line 7, figure 1 --	1-17
A	US 5400741 A (GEORGE T. DETITTA ET AL), 28 March 1995 (28.03.95), figures 1-7 --	1-17
A	US 5531185 A (KOJI ASANO ET AL), 2 July 1996 (02.07.96), figures 8-9, abstract --	1-12

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 12 June 1998	Date of mailing of the international search report 30 -06- 1998
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Mårten Hulthén Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00051

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5096676 A (ALEXANDER MCPHERSON ET AL), 17 March 1992 (17.03.92), figures 1-2, abstract --	1-17
A	EP 0553539 A1 (SCHERING CORPORATION), 4 August 1993 (04.08.93), figures 1-7 --	1-17
P,A	EP 0780496 A1 (DORNIER GMBH), 25 June 1997 (25.06.97), figure 3 -- -----	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

09/06/98

International application No.

PCT/NO 98/00051

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US	5505916	A	09/04/96	NONE	
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